Chem Ed

EDITORIALLY SPEAKING

A year ago we used this page for some comments about continuity and change. Readers will recall that we tried to point out that the only continuity appropriate for THIS JOURNAL is a policy of making changes. This month we would like to say these things again, at least by implication, as we acknowledge the important role of the Editorial Board. First and foremost in our thinking is the huge debt of gratitude we owe these men. Without their advice and help, our Editor's lot would be a sorry one. We feel that readers should know more than merely the names of these men who contribute so much to THIS JOURNAL.

Completing terms of service on the Editorial Board are Laurence S. Foster, Henry M. Leicester, and Arthur H. Livermore.

Elsewhere in this issue, Larry Foster's fellow members of the New England Association of Chemistry Teachers pay tribute to his long and faithful service as editor of the "Report." Two editors of THIS JOURNAL have counted on him and valued his advice. The steady stream of papers so useful to teachers of high school chemistry which has appeared under the NEACT banner is due to the discerning Foster eye. An outstanding teacher, now a director of metallurgical research, Larry has always been willing when called on for book-reviewing or manuscript refereeing. Readers never will know how many submitted periodic tables have not reached the printed page because of his keen ability to separate the useful from the merely pretentious.

The role of the history of chemistry in the background of the successful teacher is one of the concerns of the members of the Division of History of Chemistry of the American Chemical Society. As a representative of that Division, Henry Leicester, Professor of Chemistry at the College of Physicians and Surgeons in San Francisco, also has served two editors as a consultant on historical matters. He is known the world over as an author of outstanding scholarship in the history of chemistry and as editor-in-chief of *Chymia*. His generous willingness to assume a share of our editorial problems on top of his first-line duties is the mark of a dedicated scholar-educator.

Reed College in Portland, Oregon, is one of the nation's liberal arts colleges always mentioned on lists of institutions noted for excellence in science instruction. Arthur H. Livermore, a product of that school and now on its faculty, is one of the chief reasons for its continued excellence. A biochemist by training, his teaching and research have led him in many directions, notably in applications of radiochemical techniques. In recent years he has been one of the co-directors of the exciting experiment in the teaching of high school chemistry, "The Chemical Bond Approach." Turning to him for advice is a habit we know we cannot break merely by allowing his official term on the Board to end.

The four new names on the list of the Editorial Board, Robert D. Eddy (Tufts University), Aaron J. Ihde (University of Wisconsin), S. Z. Lewin (New York University), and John J. McKetta (University of Texas), all are known to readers through the pages of THIS JOURNAL.

The duties of associate editor for the NEACT Report section are being taken over by R. D. Eddy. Long active in that organization, he has served as President and a director of its Summer Conference. Physical and general chemistry are the focus of his interest. He has had an active part in planning the innovations of the Tufts curriculum in chemistry.

Aaron J. Ihde is another chemist-historian known and respected both by generalists and specialists in two disciplines. Wisconsin born and trained, a former Carnegie Fellow at Harvard, he and his students have contributed widely to the scholarship of chemical history. Readers of these pages recall his careful analysis of the developments of chemical concepts so useful to teachers.

Few features in the JOURNAL OF CHEMICAL EDUCATION have produced the enthusiastic reader response that "Chemical Instrumentation" has. This monthly feature will continue at least for another year. The author, S. Z. Lewin of Washington Square College of NYU, has wide experience with a variety of instruments and their applications. A New Yorker by birth and collegiate training, he earned graduate degrees at Michigan and served in the chemical warfare service before returning to the canyons of Gotham. His research and teaching span a wide range of physical and analytical chemistry.

John J. McKetta, Professor and chairman of the Department of Chemical Engineering at the University of Texas, succeeded to that post on the death of his former colleague, Kenneth A. Kobe. The Editor of THIS JOURNAL is delighted that Dr. McKetta also is willing to fill the gap in the Journal family left by Dr. Kobe's passing. Not only is his background of industrial experience and chemical engineering instruction a valuable addition to our editorial resources, but his having wielded the editorial blue pencil on the *Petroleum Refiner* for a period of years is an association for which any editor would give special thanks.

D. B. Sowerby
and **L. F. Audrieth**[1]
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Inorganic Polymerization Reactions

I. Condensation Polymerization

Modern technological demands for compositions of matter which have desirable mechanical and use characteristics at increasingly higher temperatures as well as at low and ambient temperatures have directed the attention of investigators to systems which are either strictly inorganic or inorganic-organic in character (*1*). Efforts are now being made to develop polymeric materials (thermosetting and thermoplastic substances, elastomers, adhesives, coatings, hydraulic fluids, etc.) which contain skeletal frameworks involving linkages between elemental species other than carbon.

Although polymerization phenomena have usually been associated with organic chemical processes, there are many instances where simple inorganic substances can be converted from smaller molecular or ionic units into larger aggregates. However, with the increasing emphasis on the application of structural concepts and with the use of experimental methods and procedures which help to define more precisely the structures of molecules and ions, modern inorganic chemistry has become more and more the chemistry of matter in a highly polymerized state.

The marked influence of the structural and organizational concepts of organic chemistry upon the development of inorganic chemistry is self-evident. In the first place it was not until the inorganic chemists followed their organic colleagues into the realm of structural chemistry that real progress was seen. Secondly, the properties of inorganic aggregates can be modified through introduction of organic groups and radicals so that the advantages of both organic and inorganic systems can be incorporated into a single substance. The silicone type polymers may be cited as examples. And finally, the experimental methods useful for preparing organic polymers can be adapted to inorganic systems. It is the purpose of this presentation to direct attention primarily to polymerization processes, rather than to the products themselves.

There are three principal categories of inorganic reactions which lead to the formation of substances of higher molecular weight: *condensation* reactions which involve the elimination of simple molecules, *addition* reactions in which the monomeric, low molecular weight units are caused to react with themselves to yield polymeric products, and *coordination* polymerization processes which, although frequently classified under both condensation and addition polymerization, are sufficiently distinctive to warrant separate treatment.

This paper will explore various classes of condensation reactions; subsequent articles in this series will be concerned with the formation of higher molecular weight species through addition polymerization reactions and through coordination processes.

Condensation polymerization reactions are essentially "desolvation" processes, resulting in the formation of higher molecular weight products through the elmination of simple molecules. Such condensation reactions may be subdivided into a number of different classes.

Cationic and Anionic Aggregation in Solution

These processes involve essentially the elimination of water to form hydroxo and/or oxo complexes. Cationic aggregation is favored by the addition of base and may lead to the eventual precipitation of hydroxides or hydrous oxides. Anionic aggregation, on the other hand, leads to the formation of polyanions by a process which involves the elimination of water from protonated species. Anionic aggregation may lead eventually to the precipitation of non-metallic oxides or of hydrated acidic oxides. Although we normally limit consideration of such reactions to those which occur in aqueous solutions, similar processes take place in non-aqueous systems, such as ammonia, acetic acid, and the alcohols.

Cationic Aggregation

The precipitation of an insoluble hydroxide by addition of base to a solution containing a polyvalent metallic ion is usually represented by a simple ionic equation:

$$M^{+3} + 3\,OH^- \rightarrow M(OH)_3$$

Such precipitation reactions frequently take place with formation of so-called basic salts; in other instances a considerable amount of base can be added before precipitation occurs. If such hydrated metallic ions, especially those characterized by high charge and small size, be looked upon as typical cationic acids from the Brønsted-Lowry point of view, it becomes apparent that the following acid-base equilibrium is quickly established in water:

$$\underset{\text{Acid}}{M(H_2O)_6^{+++}} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Base}}{[M(OH)(H_2O)_5]^{++}} + \underset{\text{Acid}}{H_3O^+}$$

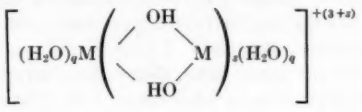
Based upon a paper presented before the Division of Polymer Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

Sponsorship of these studies through a grant from the National Science Foundation, NSF-G-2743, is acknowledged with gratitude.

This is the first in a series of three papers on this topic to be published in the JOURNAL OF CHEMICAL EDUCATION. Subsequent articles will be concerned with the formation of higher molecular weight species through addition polymerization reactions and through coordination processes.

[1] At present, serving as Scientific Attaché at the American Embassy, Bonn, Germany.

Such an equilibrium can be displaced by addition of base to yield a hydroxo-aquo-metallate complex as an intermediate species. Physicochemical studies of such systems have shown, however, that aggregation takes place presumably through two consecutive processes. The first involves *olation*, that is, the formation of relatively unstable bridged hydroxo complexes, followed by a second step which is referred to as *oxolation* and in which oxo bridges are believed to constitute the links between the metallic atoms. The existence of poly nuclear species, represented by formulas of the type

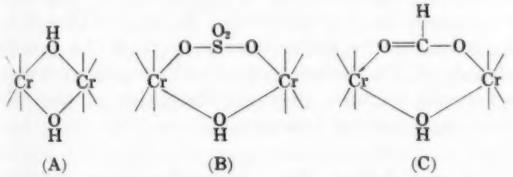


or

$$(M_nO_{n-1})^{+(n+2)}\cdot xH_2O$$

must be postulated. The average degree of polymerization varies and usually increases rapidly with increasing concentration of metal ion and rise in *p*H. Hydrolysis of Al^{+3}, Sc^{+3}, Th^{+4}, In^{+3}, Bi^{+3}, Fe^{+3}, Cu^{+2}, U^{+4}, UO_2^{+2} gives rise to polymeric cations. Pokras (*2*) and Sillén (*3*) have reviewed this subject, and the work of Kraus (*4*), Connick (*5*), and Kilpatrick (*6*) can also be consulted for further details.

The importance of such aggregation processes in the preparation of chrome-tanning solutions has been the subject of considerable investigation (*7*). Up to one mole of base per mole of Cr(III) ion may be added before precipitation occurs. It has been found that the addition of certain compounds brings about enhanced stability of such solutions, especially if such addends make available anionic species that may also be considered to serve as bridging groups. The four-membered diol rings (A) are therefore believed to be less stable than six-membered ring systems which are presumed to form when sulfate (B) or formate (C) are present in such solutions. The bidentate sulfato and formato ligands do not participate readily in reactions leading to oxo complexes. Other bidentate groups may also take part in the formation of cationic aggregates (*8*).



(A) (B) (C)

Particularly interesting are the commercial products sold under the trade names of Quilon and Volan (*9*, *10*), respectively, in which it is assumed that stearato and methacrylato groups act as bridging units. These Cr(III) complexes are depicted in Figure 1 as existing in the non-ionic state in non-aqueous systems such as the alcohols and acetone, in the aquated state in aqueous solutions, and in the olated or oxolated state after such solutions have been heated, or aged, or modified by raising the *p*H. The actual structures of many of these products are not known, but somehow the soluble products, which are used for various surface applications, always contain chromium and the hydroxo and carboxylato groups in the mole ratio 2:1:1 in the form of a cationic complex.

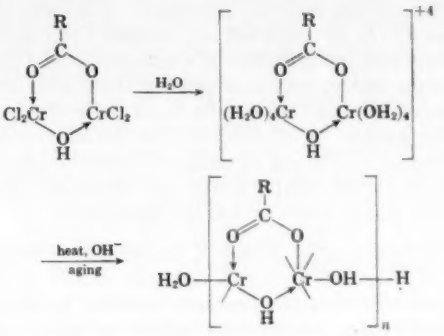


Figure 1.

When the diluted solution containing the complex is applied to a substrate and then heated, further polymerization occurs to give an insoluble coating which will firmly attach itself to negatively-charged surfaces containing polar groups, presumably both by covalent bonds and by polar forces. Surfaces which contain the OH, NH_2, COOH, $CONH_2$, and SO_3H groups, are particularly susceptible to strong bond formation. Bonding between "Volan" methacrylato chromic

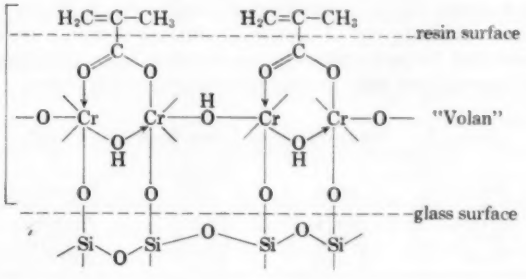


Figure 2.

chloride and the surface of a glass fiber is indicated in Figure 2. Bonding to glass takes place presumably to give a chromium-oxygen-silicon bond; the vinyl grouping of the methacrylato group develops compatibility and reactivity of such a coating with vinyl resins. It is thus possible to bond a resin, through the chromium-methacrylato complex, to glass. The substituents on the carboxylato group, represented by R in Figure 1, can be varied widely in order to achieve specific surface effects. Patents have been issued covering the use of acids in which R is $HOCH_2$, $CNCH_2$, Cl_3C, $R'CH_2$, $(H_3C—)(H_2C=)C—$ and 2:4 dihydroxyphenyl. One can only speculate whether or not other acids can be used in the same way.

It seems evident from a purely mechanistic point of view that all processes leading to the eventual precipitation of a hydroxide or hydrous oxide of a polyvalent metallic ion must involve stepwise reactions. The question now arises whether such reactions are not also possible in non-aqueous systems in which the solvated polyvalent ion may also be considered to react as an acid, with various basic entities. Some work along this line has already been accomplished by Schmitz-Dumont (*11–14*) in his study of the amides of chromium-(III), cobalt(III), titanium(III), thorium(IV), and

other like species in liquid ammonia. The ammoniated cations are to be regarded as cationic acids in liquid ammonia and, on addition of amide ion in the form of potassium amide, may undergo reactions with the formation of ammono basic salts or of the corresponding metallic amides. The structures for the latter could be regarded as consisting initially of μ-amido aggregates which at higher temperatures lose ammonia to form the more stable imido or nitrido aggregates.

$$\underset{\text{Acid}}{[M(HX)_n]^{+z}} + \underset{\text{Base}}{HX} \rightleftharpoons \underset{\text{Acid}}{HX{\cdot}H^+} + \underset{\text{Base}}{[M(HX)_{n-1}X]^{(z-1)+}}$$

It is probable that the acetates of many metallic ions of high charge and small size can likewise be represented better as polymeric cationic species containing bridged acetato groups. This certainly is indicated by results of a recent investigation on the products formed when oxides are dissolved in 100% acetic acid containing acetic anhydride (*15*). The normal acetates are not obtained, but in their place products slowly precipitate from solution which are assumed to be hydroxo or oxo compounds. The alkali metal alcoholates also act as strong bases in the alcohols which can be looked upon as water-like solvents. Many of the metal alcoholates have been found by Wardlaw, Bradley, and co-workers (*16*, *17*) to be polymeric in character. Since reactions entailing formation of solvo bases in non-aqueous systems (Table 1) have been worked out so thoroughly and shown to be so consistently similar in character to those which apply in aqueous solution, it would seem desirable to undertake a more detailed scientific study of aggregation phenomena in non-aqueous systems.

Table 1. Precipitation of Solvo-Basic Compounds

Solvent	Base	Solvated ion	Solvo-base
HOAc	NaOAc	Cu^{++}	$Cu(OAc)_2$
HNH_2	KNH_2	Cr^{+++}	$Cr(NH_2)_3$
HOR	NaOR	Al^{+++}	$Al(OR)_3$

Anionic Aggregation

The processes whereby polyanionic aggregates, iso- and heteropoly acids and hydrated (or hydrous) nonmetallic oxides (sols and gels), are formed may also be regarded as acid-base reactions from the Brønsted-Lowry point of view. The simple anions act as bases and are capable of protonation; many of these protonated species undergo stabilization by aggregation with the elimination of water. It is even conceivable that such stabilization processes also involve formation of olated intermediates. For aqueous solutions of chromates, the aggregation reactions can be represented by the following equations:

$$CrO_4^= + H^+ \rightarrow [HCrO_4^-]$$
$$2[HCrO_4^-] \rightarrow Cr_2O_7^{=}\text{–}Cr_2O_7^= + H_2O$$
$$nCrO_4^= + 2nH^+ \rightarrow (CrO_3)_n + nH_2O$$

Similar equations involving a larger number of intermediate water-soluble polyanionic species can be written for the processes which occur when the *p*H of solutions of molybdates, tungstates, and vanadates is gradually lowered (*18*, *19*, *20*). Consumption of protons occurs during these aggregation reactions. For these examples polymerization and depolymerization reactions usually take place rapidly. Addition of base to polyanionic or heteropolyanionic species brings about rapid depolymerization to the monoanionic components.

Phenomena which characterize silicate and silicic acid systems are of particular interest and importance (*21*). The state of aggregation of the silicate ion is determined by the *p*H of the medium. A simple ionic species, variously described as the metasilicate, $HSiO_3^-$, the hexahydroxosilicate, $Si(OH)_6^=$, or the aquo-pentahydroxosilicate ion $[Si(OH)_5(H_2O)]^-$, is believed to exist in strongly alkaline solution (above *p*H 13.6). A di-silicate species, which may be a "diol" aggregate or a siloxane moiety, characterizes solutions from *p*H 13.6 to 10.9. Below *p*H 9 the state of aggregation varies with time and with temperature; colloidal systems come into existence. These may "coagulate" or "aggregate" at rates depending upon environmental factors. Gelation may also occur. A "fibrillar" concept is now popularly accepted in describing such gels, the assumption being that such fibrils are composed of large"polysilicic acid" molecules.

Proposed mechanisms for the polymerization of silicate ions (or of silicic acid, or hydrated silica) differ only with respect to the nature of the reactive hexacovalent intermediate. The argument depends largely upon whether the $Si(OH)_6^=$ ion *really exists*, or reaction of silicic acid with hydroxide ion (and concomitant aquation) results in the temporary formation of a hexacoordinated species, $[(H_2O)Si(OH)_5]^-$. In either case intermediate olated structures are believed to form subsequently; loss of water from the silanol groups of the postulated diol complex gives rise to the random formation of siloxane linkages. Continuation of these processes could lead to the observed aggregation phenomena and eventually to gelation. The whole mechanism is analogous in principle to the reactions involved in the aggregation of polyvalent aquated metallic ions and of the anions to which reference has been made above.

Solutions of monomeric or low molecular weight silicic acids are, in effect, supersaturated solutions of hydrated silica and are produced by the hydrolysis of silicon halides, silicate esters or by treatment of a soluble silicate with acid or an acid ion exchange agent so that the *p*H of the resulting solution is near 3. Polymerization can be inhibited by addition of hydrogen bonding agents which of themselves do not affect the hydrogen ion concentration. It appears that dipole orientation of the donor species toward the positive hydrogen of the silanol group blocks tendency toward olation and, in turn, prevents formation of the more stable oxo (siloxane) linkages.

Cationic and Anionic Aggregation Reactions at Higher Temperatures

Cationic aggregation at higher temperatures in the absence of solvent leads to the formation of basic salts and, eventually, of polymeric oxides from hydrated salts by the elimination of water and/or other acidic components. Such cationic aggregation reactions are not so well understood as the corresponding reactions of anionic aggregation, which involve dehydration polymerization processes to yield polyanionic aggregates whose size (ionic weight) depends both upon the potential acidity of the simple anions and upon the temperatures maintained during the aggregation. Reactions of anionic aggregation among the hydrogen

phosphates, leading to the poly- and polymetaphosphates, have been studied extensively.

Cationic Aggregation

One of the difficulties involved in the preparation of anhydrous salts of polyvalent metallic elements is the formation of so-called basic salts from the hydrated species. This is especially true when an attempt is made to prepare anhydrous salts from hydrated halides. Not only can water be eliminated by thermal dehydration but in many instances the volatility of the hydrogen acid is a factor which must be considered. The end products are frequently given formulas such as $MgO \cdot MgCl_2$, or NdOCl. The true nature of these compounds has not really been defined, but the fact remains that elimination of water and of volatile acid results in the formation of aggregates which must contain oxo linkages, since these substances approach the oxides in composition.

Anionic Aggregation

The "condensed" phosphates, the pyro-, tri-, meta-, and poly-phosphates, are manufactured commercially by high temperature dehydration procedures. All these condensation reactions represent polymerization processes which involve interactions of *protonated* phosphate ions. Even in aqueous solutions these ions may be looked upon as anionic acids. It is significant, however, that the mono- and dihydrogen phosphate ions are stable species in aqueous solution, in contrast to other protonated anions whose existence as intermediates in anionic aggregation processes is merely transient.

We have found it convenient to look upon such aggregation reactions as dependent upon the potential acidity of the system. This is brought out in the following series of equations in which the $H^+/PO_4^{=}$ ratio is given for each reaction. The higher this ratio, that is, the more acidic the system, the greater is the extent of aggregation which takes place on heating (*22*).

	Ratio H^+/PO_4^{-3}
$2HPO_4^{=} \rightarrow P_2O_7^{-4} + H_2O$	1/1
$2HPO_4^{=} + H_2PO_4^{-} \rightarrow P_3O_{10}^{-5} + 2H_2O$	4/3
$n\ H_2PO_4^{-} \rightarrow (PO_3^{-})_n + n\ H_2O$ (where n = 3,4 and higher)	2/1

Even though no solvent is employed, the reactions in which these anionic acids participate correspond in every way to those of the protonated species that are postulated as intermediates in the aggregation of molybdate, tungstate, vanadate, and chromate ions in solution.

Experimentally, it has been shown that protonic, cationic, and anionic acids as well as non-protonic Lewis acids can bring about such aggregation reactions at higher temperatures in the absence of solvent. The alkali hydrogen sulfates, by virtue of the fact that they contain the anionic acid, the HSO_4^- ion, are capable of converting orthophosphate to pyrophosphate or metaphosphate at higher temperatures. When allowed to react with disodium hydrogen phosphate at temperatures around 200°C, the hydrogen sulfate converts the latter into disodium dihydrogen pyrophosphate (*23*). Ammonium nitrate, serving as a source of the ammoniated proton, will on fusion with disodium hydrogen phosphate bring about conversion of the latter to trimetaphosphate. Sulfur trioxide, a typical Lewis acid, will displace P_4O_{10} from potassium pyrophosphate at higher temperatures (*24*).

It should be recalled that the depolymerization of polyanionic species in aqueous solutions of polytungstates, polychromates, etc., takes place very rapidly when base is added. Similar depolymerization processes also occur in high temperature, non-solvent systems. Fusion of the highly polymeric "hexametaphosphate" with metallic oxides, with sodium sulfide, and with sodium fluoride in which the oxide, sulfide, and fluoride ions function as anionic bases, results in depolymerization to the orthophosphate, the monothioorthophosphate, and the fluophosphate, respectively (*25*).

Desolvation Processes at Higher Temperatures

Thermal desolvation reactions are related to the processes described above. The aggregation of hydroxides and/or hydrous oxides to polymeric oxide structures has been studied extensively. More striking and less well known are the deammonation reactions which characterize the processes that occur when more highly ammoniated derivatives of certain non-metallic elements are heated. The phosphino-borines and related substances polymerize on heating with elimination of hydrogen; consequently reactions of this type are also included among thermal condensation processes.

Dehydration

Many hydrous oxides, hydroxides, and oxy acids of polyvalent elemental species undergo thermal dehydration reactions. Such processes may lead eventually to highly polymeric oxides. There are instances, however, where formation of the anhydrous oxides is difficult to accomplish, even though aggregation takes place as in the dehydration-condensation of phosphoric acid. Depending upon the length of time and the temperature of heating, phosphoric acid can be converted into various equilibrium mixtures of poly- and polymetaphosphoric acids (*26*). Such mixtures can also be made by dissolving P_4O_{10} in phosphoric acid and heating to "equilibrate" the product. Conversely related to these aggregation processes are the stepwise hydration-depolymerization reactions which, in the case of P_4O_{10}, lead to formation of the intermediate poly- and metaphosphoric acids (*27*).

Deammonation

Deammonation processes may involve the loss of ammonia from molecules, from cationic species, and from anionic species. Examples of such processes follow.

Molecular Deammonation. The deammonation of silicon tetramide is believed to go through a number of steps to give a series of more highly condensed ammono derivatives and, finally, silicon nitride (*28*, *29*). Phosphorus oxytriamide can be made by the ammonolysis of phosphorus oxytrichloride (*30*). Loss of ammonia is observed when this material is heated above 80°C in high vacuum to give a variety of condensation products. At a temperature of 600°C, highly polymeric phosphorus oxynitride results (*30*). Klement and Bär (*31*) have recently shown that compounds with the general

formula $P_xO_x(NH)_{x-1}(NH_2)_{x+2}$ where $x = 2$–6, result when phosphorus oxytriamide is deammonated at temperatures in the region of 100°C under atmospheric pressure.

$$Si(NH_2)_4 \rightarrow [Si(NH)_2]_n \rightarrow [Si_3N_4]_n$$
$$PO(NH_2)_3 \rightarrow P_xO_x(NH)_{x-1}(NH_2)_{x+2} \rightarrow (PON)_n$$
$$[PN(NH_2)_2] \rightarrow (PNNH)_n \rightarrow (P_3N_5)_n$$
$$SO_2(NH_2)_2 \rightarrow HN(SO_2NH_2)_2 \rightarrow (HNSO_2)_3$$
$$CO(NH_2)_2 \rightarrow HN(CONH_2)_2 \rightarrow (HNCO)_3$$

The reaction of PCl_5 with ammonia leads to the formation of phosphonitrilamides of undefined molecular complexity. These substances can be deammonated by heating to give phospham whose composition may be represented by the empirical formula, $(HNPN)_n$. At still higher temperatures the latter loses ammonia to approach the composition of the highly polymeric triphosphorus pentanitride (*32*). Sulfamide loses ammonia at approximately 160°C to form imidodisulfamide, the biuret analog in the sulfuric acid system (*33*); at approximately 209°C it is converted into the ammonium salt of trimeric sulfimide (*34*). These reactions remind one of the deammonation of urea to biuret and to cyanuric acid.

Cationic Deammonation. Such reactions have been studied in particular by Schmitz-Dumont (*11–14*). Thus, for instance, hexamine chromium amide undergoes loss of ammonia on heating to form the highly polymeric nitride. The intermediate deammonation products are presumed to consist of a network of amido and/or imido groups linking together chromium atoms in a three-dimensional polymeric structure.

Anionic Deammonation. Examples of deammonation reactions entailing anionic species have been studied by Klement and Biberacher (*35*, *36*). The sodium salt of phosphoramidic acid loses ammonia with condensation to a pyrophosphate-like species in which the POP bond is replaced by a PNP bond. The sodium salt of phosphorodiamidic acid loses ammonia in like fashion to go over into what may be regarded as a polyamido metaphosphate. It is highly probable that salts of other ammono and mixed aquo ammono acids will be found to undergo deammonation condensation at higher temperatures to give polymeric anionic species in which the central atoms are linked together by imido or even by nitrido groups.

$$2(NaO)_2PONH_2 \xrightarrow{\Delta} Na_4P_2O_6(NH) + NH_3$$
$$n NaOPO(NH_2)_2 \xrightarrow{\Delta} [NaOPO(NH)]_n \text{ or } (NaPO_2NH)_n + n NH_3$$

Such deammonation-condensation reactions can also be carried out by use of an acidic desolvating agent. It has been shown by Becke-Goehring (*37*) that phosphorus oxytriamide, at low temperatures in ether suspension, reacts with gaseous hydrogen chloride to undergo condensation to an imido-diphosphoric tetramide.

$$2PO(NH_2)_3 + HCl \rightarrow (H_2N)_2PO(NH)PO(NH_2)_2 + NH_4Cl$$

Dehydrogenation (Borine Polymers)

One of the main points of interest in compounds containing boron-nitrogen linkages arises from the fact that these elements straddle carbon in the periodic table. A boron and a nitrogen atom bound together have the same number of electrons as two carbon atoms, and the sizes of the two pairs of atoms are approximately the same. These facts are reflected in the similarity in physical properties between certain boron-nitrogen compounds and the corresponding substances containing only carbon atoms. Interest in these compounds has led to the study of analogs containing phosphorus and arsenic instead of nitrogen. They are discussed here as examples of condensation reactions brought about by the elimination of hydrogen.

Diborane forms addition compounds at low temperatures with phosphine and substituted phosphines (*38*) These adducts are susceptible to two modes of thermal decomposition, (*a*) disproportionation and (*b*) elimination of hydrogen with the formation of intermediates which stabilize by polymerization. The product of the reaction between phosphine and diborane when heated at 65°C for long periods of time, gives hydrogen and a white, insoluble polymeric compound analyzing as $PBH_{3.75}$. The ideal formula is probably PBH_4, the low hydrogen content arising from a dehydrogenation process with the formation of occasional cross-linkages between $(PBH_4)_n$ chains.

The dimethyl phosphine-diborane addition compound $(CH_3)_2PH{\cdot}BH_3$, when heated at 150°C, produces a series of polymeric compounds, separable by fractional sublimation in high vacuum. The most stable compound is a trimer $[(CH_3)_2PBH_2]_3$ together with smaller quantities of a tetramer and a long chain polymer. Although these compounds contain boron-hydrogen bonds, they are curiously stable toward attack by both acids and bases. Hydrolysis takes place only slowly even when the compounds are heated with acids at 300°C in sealed tubes. The addition compound $(CH_3)_2PH{\cdot}HB(CH_3)_2$ disproportionates when heated before appreciable hydrogen is eliminated, but a trimeric compound $[(CH_3)_2PB(CH_3)_2]_3$ has been prepared from dimethyl phosphine and dimethyl boron bromide in the presence of triethylamine. The compound melts at 333°C and is stable in the presence of moisture, acids, and bases. In this series of compounds, an increasing degree of methylation seems to stabilize the primary addition compound, whereas the hydrogen elimination reaction becomes more difficult to perform. It is also apparent that only dimethyl phosphinoborines are more stable as trimers than higher polymers.

The arsine compounds are very similar to the corresponding phosphine derivatives, except that the bonds involving arsenic are weaker than those with phosphorus (*39*). For example, there is no reaction between arsine and diborane at −78°C, but if the mixture is warmed to room temperature, hydrogen is evolved with the formation of an insoluble polymeric material of ideal composition $AsBH_4$. More hydrogen is evolved as the temperature is raised and this is attributed to cross-linking between chains as in the case of $(PBH_4)_n$. Methyl arsine with diborane on heating gives a polymer which analyzes as $CH_3AsB_{1.01}H_{2.90}$.

The reaction with dimethylarsine completely parallels the dimethylphosphine reaction in giving trimeric, tetrameric, and long chain polymers of $(CH_3)_2AsBH_2$. In this case, however, appreciable hydrogen evolution was detected at 50°C while in the phosphine reaction the temperature had to be raised above 100°C.

Hydrogen sulfide reacts very slowly (*40*) with diborane at room temperature, but after 140 days a transparent glassy polymer with empirical formula

HBS was obtained. Methyl mercaptan on the other hand, forms an unstable adduct at −78°C which loses hydrogen spontaneously when warmed to room temperature. A white insoluble solid remains which, from vapor pressure studies appears to be a mixture of easily interconvertible polymers. No separation could be effected and decomposition occurred at 140°C.

Solvolytic Reactions

These are processes in which a solvent-sensitive starting material undergoes partial solvolysis with the formation of actual or hypothetical intermediate species, which by subsequent desolvation reactions are converted into higher molecular weight products. Emphasis in these processes is placed on products obtained by partial solvolysis.

All too frequently we are inclined to oversimplify processes of solvolysis of polyvalent non-metallic halides, oxyhalides, thiohalides, and even esters by assuming that only complete solvolysis can occur. We think of the hydrolysis of compounds like silicon tetrachloride, phosphorus (V) oxychloride, and sulfuryl chloride in terms of the formation of silicic acid, phosphoric acid, and sulfuric acid, largely because we generally add these very reactive halides to a large excess of water. We then go further to justify our experimental observations by tacitly assuming that the high reactivities of the attached halogen atoms preclude the isolation of partially solvolyzed products. We now know, however, that such reactions take place in a stepwise fashion and that simple intermediate, as well as highly condensed, solvolysis products can be obtained if the proper experimental conditions are employed. Reactions of partial solvolysis can be achieved under one or more of the following conditions:

(*a*) by reaction at lower temperatures,

(*b*) by addition of the solvolytic agent to the reactive halogen compound so that the latter is always present in excess,

(*c*) by use of a solvent in which the reactivities of one or both reactants is reduced,

(*d*) by reducing the concentration or the reactivity of the solvolytic agent through use of solvates or onium salts, and

(*e*) by using systems in which small concentrations of the solvolytic agent are formed continuously throughout the course of a chemical reaction.

When, therefore, a solvolytic agent is employed which in itself contains more than one replaceable hydrogen atom (such as water or ammonia), it becomes possible for the product of partial solvolysis to react with the unchanged halogen compound to undergo condensation polymerization to form species of higher molecular weight. The examples which are presented below suggest that this is one of the most promising, yet least thoroughly explored, approaches to the formation of inorganic aggregates. Insofar as these product mixtures still contain reactive halogen atoms, it becomes possible by appropriate further reactions to replace these active groups by organic or inorganic moieties, and even to effect further condensation reactions.

Partial Hydrolysis

Both Schumb (*41*) and Goubeau (*42*) have examined the partial hydrolysis of silicon tetrachloride at low temperatures; fractionation of the products at low pressures gave a series of condensed chlorosiloxanes with the general formula $Si_nO_{n-1}Cl_{2n+2}$ as oily liquids with values of n up to six. In effecting partial solvolysis of silicon tetrachloride, it seems reasonable to assume that chlorosilanols are formed as intermediates and that these may then undergo condensation with each other, or with excess silicon tetrachloride, to bring about aggregation to chlorosiloxanes.

$$SiCl_4 + H_2O \rightarrow Cl_3SiOH + HCl$$
$$Cl_3SiOH + ClSiCl_3 \rightarrow Cl_3SiOSiCl_3 + HCl$$
$$Cl_3SiOSiCl_3 + HOSiCl_3 \rightarrow Cl_3SiO\text{-}SiCl_2\text{-}O\text{-}SiCl_3 + HCl, \text{ etc.}$$

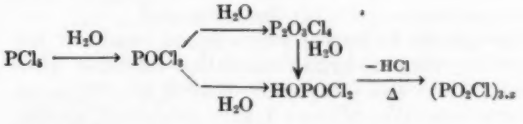
Ether as a solvent could be regarded as exerting a beneficial effect by removing hydrogen chloride as a solvate, $Et_2O{\cdot}HCl$, thus facilitating solvolysis at low temperatures.

These compounds and the corresponding oxybromides have also been prepared by passing a mixture of oxygen and the halogen over silicon heated to approximately 700°C (*43*, *44*). In addition to the chain polymers, a crystalline, cyclic tetramer, $(SiOX_2)_4$ was also obtained in each case.

The partial solvolysis of hexachlorodisilane would be expected to give a series of compounds with the type formula $Si_{2n+2}O_nCl_{4n+6}$. Only the first member, Si_4OCl_{10}, was actually isolated (*45*). There is evidence for formation of higher members of this series, but these apparently suffered decomposition when submitted to fractional distillation. The only other isolable compound was $Si_5O_2Cl_{12}$, presumably obtained through the loss of silicon and chlorine from the second homolog, $Si_6O_2Cl_{14}$.

With germanium tetrachloride (*46*), controlled hydrolysis gave only a highly polymeric compound represented by the empirical formula $Ge_2O_3Cl_2$. However, the first member of the expected series of oxychlorides, Ge_2OCl_6, is known. The polymer may have a fibrous structure, similar to that postulated for $Ge_2O_3(i\text{-}PrO)_2$.

A well-known example of a stepwise hydrolysis reaction entails the preparation of phosphorus oxychloride from phosphorus pentachloride. Only one other intermediate compound, pyrophosphoryl chloride, $P_2O_3Cl_4$, had previously been isolated by further hydrolytic action. Complete hydrolysis leads to phosphoric acid. Recently, however, dichlorophosphoric acid has been isolated as the principal low temperature hydrolysis product of both phosphorus oxychloride and pyrophosphoryl chloride (*47*). Dichlorophosphoric acid undergoes decomposition with loss of hydrogen chloride at higher temperature to give a mixture of metaphosphoryl chlorides from which the trimer, $(PO_2Cl)_3$ has been isolated and identified.

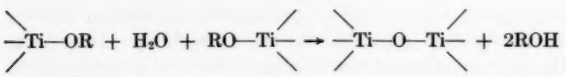


Alcoholysis

Alcohols have been used as solvolyzing agents, though mainly for the preparation of completely substituted compounds. The products of these reactions are for the most part liquids, often with high boiling points, though waxes and low melting solids are sometimes formed. Molecular weight determinations, both

by cryoscopic and ebullioscopic methods, have led to formulas of varying molecular complexity. In the case of titanium tetraethoxide (*48*) the complexity, as determined from the depression of the freezing point of benzene, rises from unity at near zero concentration to approximately three at mole fractions above 0.01. This polymerization is attributed to the fact that titanium is coordinatively unsaturated in the tetraalkoxides. Zirconium, with coordination number eight, might be expected to form even larger aggregates, but the complexity for the tetraethoxy derivative is only 3.6 in boiling benzene. As complexity has been shown to decrease with increasing temperature, it has been suggested that this compound at normal temperatures exists as a pentamer in which zirconium exhibits a coordination number of six. In the case of thorium (*49*), which can also show a coordination number of eight, the complexity of the normal alkoxides averages about 6.3 monomer units. The smallest possible unit, based on the coordination of eight groups, would be an octamer, consisting of eight cubes arranged in a flat ring.

The alkoxides react readily with water, giving products which vary in composition and complexity with, among other factors, the amount of water used. Bradley, Gaze, and Wardlaw (*50*) have recently made a comprehensive study of the hydrolysis reactions of various titanium alkoxides, both by the usual analytical methods and by an ebullioscopic technique. The primary process, involving the consumption of water, appears to take place rapidly; since the products of hydrolysis were found to contain few if any hydroxyl groups, the reaction is probably best represented by the partial equation:



In the case of titanium ethoxide, depending on the water-titanium ratio, crystalline compounds have been obtained analyzing as $Ti_6O_4(OEt)_{16}$ and $Ti_{12}O_{12}(OEt)_{24}$. An insoluble compound, $Ti_3O_4(OEt)_4$, was precipitated when the ratio reached 1.75. Bradley and co-workers have explained the formation of these compounds on the basis of a triple chain polymerization reaction involving the trimeric form of titanium tetraethoxide as the basic unit. Such reactions would result in the retention of the coordination number six for each titanium atom and would explain the absence of Ti-OH bonds. The general formula $Ti_{3(x+1)}O_{4x}(OEt)_{4(x+3)}$ can be assigned to a series of polymers of this type and is in agreement with the compounds isolated. Further the theory predicts the ultimate linear polymer as a triple chain molecule with the empirical formula $Ti_3O_4(OEt)_4$; such a product has actually been prepared.

Although the hydrolysis products are usually of low complexity, they undergo dismutation reactions when heated. Molecules of the tetra-alkoxide are eliminated with the formation of more highly condensed species:

$$2Ti(OPr^i)_4 + H_2O \rightarrow Ti_2O(OPr^i)_6 + 2Pr^iOH$$

$$4Ti_2O(OPr^i)_6 \xrightarrow[100°C]{\text{vacuum}} 5Ti(OPr^i)_4 + [Ti_3O_4(OPr^i)_4]_n$$

Ammonolysis

Schumb has extended his work on the partial solvolysis of silicon tetrachloride to include a study of the reactions which occur when ammonia (*51*) and hydrogen sulfide (*52*) are used as solvolytic agents. Partial ammonolysis was carried out under a variety of conditions ranging from the action of ammonia gas on an ethereal solution of silicon tetrachloride at −75°C, use of $AgCl{\cdot}3NH_3$ as ammonating agent at 0°C, to a vapor phase reaction at 825°C. In all cases, solid polymeric materials of unknown composition were obtained. The vapor phase reaction led to formation of two low molecular weight chlorosilazanes, $Si_2(NH)Cl_6$ and $Si_3N_4Cl_{20}$. Besides highly polymeric materials, hydrogen sulfide gave only one isolable product considered to be a tetramer of $SiSCl_2$.

Complete ammonolysis of phosphorus pentachloride, which can be accomplished by treating the halide with liquid ammonia, results in formation of the various polymeric forms of phosphonitrilamide, $[PN(NH_2)_2]_x$ (*32*). If the concentration of available ammonia is decreased by carrying out the reaction in a solvent such as carbon tetrachloride, some phosphonitrilic chloride is produced along with the nitrilamide. A further decrease in the availability of ammonia, entailing use of ammonium chloride, leads exclusively to the formation of a mixture of phosphonitrilic chloride polyhomologs (*53*, *54*). But the phosphonitrilic chlorides still contain reactive chorine atoms and may, depending upon conditions as set forth in Figure 3, be converted into partially or completely ammonated products (*55*).

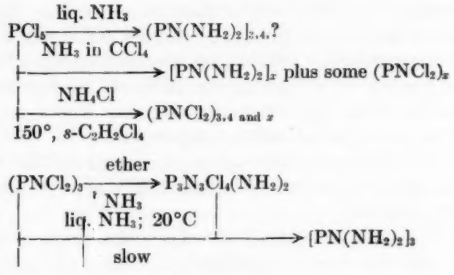


Figure 3. Ammonolysis of PCl_5

Thiosolvolysis

Reactions of solvolysis occur in many non-aqueous systems. Particularly interesting are those which have recently been carried out by Fehér and co-workers leading to the formation of the poly-sulfanes and the halo-sulfanes (*56*). By ingenious solvolytic processes, which might properly be called reactions of thiosolvolysis, i.e., appropriate interaction of sulfanes (the hydrogen polysulfides) and the chlorosulfanes, it is possible to build up compounds containing rather remarkably stable sulfur chains. The study of these chain-sulfur compounds and their ability to effect thiosolvolytic reactions has led to the characterization of the polythionic acids as sulfonated sulfanes. Thus, for instance, interaction of chlorosulfonic acid with the various sulfanes has led to the synthesis of the corresponding polythionic acids. In the same fashion, recognition of the fact that thiosulfuric acid is a monosulfonated sulfane has led Schmidt (*57*) to study the reactions of SO_3 with the higher sulfanes. A whole new series of mono-sulfonated sulfanes, a completely

new and unusual class of polythionic acids, has been isolated. The disulfonated sulfanes, which heretofore had been recognized only up to $H_2S_xO_6$ with x equal to 6, have been extended to octa, deca, and dodecathionic acids by interaction of the appropriate sulfane with SO_3. It need only be pointed out that some of the higher sulfanes such as H_2S_2 are fairly stable materials. These substances may, therefore, be expected to find greater application than ever heretofore for the introduction of sulfur chains into various inorganic and organic molecules.

$$HS_xH + ClS_yCl + HS_zH \rightarrow 2HCl + HS_x\text{-}S_y\text{-}S_zH$$
$$ClS_xCl + HS_yH + ClS_zCl \rightarrow 2HCl + ClS_x\text{-}S_y\text{-}S_zCl$$
$$HSO_3Cl + HS_xH + ClSO_3H \rightarrow HSO_3\text{-}S_x\text{-}SO_3H + 2HCl$$
$$SO_3 + H_2S_x \rightarrow HS_xSO_3H \text{ or } HSO_3\text{-}S_x\text{-}SO_3H$$

Figure 4. Examples of Thiosolvolysis (Fehér, Schmidt).

Reactions Involving Polyfunctional Inorganic and Organic Molecules

Condensation reactions between polyfunctional organic compounds are widely employed to effect formation of organic polymers. Replacement of one of the reactants by a polyfunctional inorganic compound would seem to represent an interesting approach to the formation of inorganic-organic type polymers.

Reactions of dicarboxylic acids with polyamines, of di-acid chlorides with glycols and polyamines, and of dicarboxylic acid hydrazides with dialdehydes, take place with the elimination initially, or subsequently on heating, of some simple molecule. Polyfunctional amido compounds react with formaldehyde to give intermediate methylol derivatives which on heating go over to more complex and highly cross-linked structures. Di-isocyanates react with polyamines by direct addition to form polyurethanes. The question may naturally be raised, is it possible to effect similar reactions in which one of the polyfunctional molecules is an inorganic compound and the other an organic polyfunctional reactant? Such possibilities have been evaluated only to a limited extent, yet there is enough evidence in the literature to demonstrate that such condensation processes can take place (see Figure 5).

It should be pointed out, for instance, that the formaldehyde addition reaction is not limited to compounds in which amido groups are attached to carbon atoms, but that this is specifically a reaction characteristic of the amido group regardless of the nature of the central atom (*58*). Ureaformaldehyde type polymers have been obtained by condensation of sulfamide, $SO_2(NH_2)_2$ with formaldehyde (*59*). Unpublished work by Dr. A. D. F. Toy (*60*) during his thesis research showed that resinous polymeric products can be obtained from many phosphorodiamides by reaction with formaldehyde. We have found that resinous condensation products are obtained when phosphonitrilamides and formaldehyde are allowed to react (*61*). It seems obvious that polyfunctional amido compounds containing atomic species other than carbon are capable of such condensation reactions and are worthy of more serious and thorough study.

The very interesting paper published recently by Appel (*62*) on reactions of sulfuryl di-isocyanate can be cited to show that this particular compound behaves as a polyfunctional isocyanate. It is capable of reacting with ethylene glycol to give a chain polymer. Further study of similar systems would seem to be a profitable direction for evaluation of inorganic-organic type polymeric systems.

1. $X(NH_2)_2 + CH_2O \rightarrow X(NHCH_2OH)_2 \xrightarrow{\text{heat}}$ resins

(where X = CO, SO_2, ROPO, $PO(NH_2)$, [PN])

2. $SO_2(NCO)_2 + HOC_2H_4OH \rightarrow$

$$H[OCH_2CH_2OCNHSO_2NHC]_4OCH_2CH_2OH$$

polysulfo-urethanes

Figure 5. Polyfunctional inorganic compounds.

The hydrolytic and thermal stabilities of the silicones (*63*) are believed to be due to the fact that these substances possess siloxane structures. Attempts have been made to replace some of the silicon atoms in such structures by other elements. References in the literature describe work on systems involving the following polymeric bond types:

Si—O—B (*64, 65*)	Si—O—As (*67*)
Si—O—Al (*66*)	Si—O—Sb (*68*)
Si—O—Ti (*66*)	Si—O—Sn (*69*)

To synthesize such materials processes have been used involving (*a*) cohydrolysis of mixtures of chloro-derivatives or esters, (*b*) thermal desolvation of mixtures of esters, and (*c*) condensation reactions in which one component is an organic derivative and the other a reactive inorganic compound. Like the polysiloxanes, these products represent polymeric oxide structures modified by attachment of organic groups. These substituents serve to prevent formation of completely cross-linked, rigid structures. Attempts to modify structures of other polymeric oxides, nitrides, and sulfides by similar processes would seem to offer promise of technological success.

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Films on Chemistry Teaching Aids

Three filmed lecture-demonstrations by R. T. Sanderson have recently been made available by the Bureau of Audio-Visual Instruction, Extension Division, State University of Iowa, Iowa City. These are 16mm, sound-color, about 44 minutes each, entitled:

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Rental fee is $10 per film for a 3-day period, or prints may be purchased for $275 each or $750 for the set. A supplementary booklet, "Principles and Construction of New Chemistry Teaching Aids" is supplied free with each film rental or purchase, or may be obtained separately at cost (50 cents each, or 35 cents each for 10 or more).

James F. Corwin
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Natural Quartz from the Laboratory

Natural quartz has a number of properties which have long made it a very useful material. Chemistry and geology teachers utilize the easily visible asymmetry of quartz crystals which have completed crystal faces to demonstrate the occurrence of left-handed and right-handed crystals in nature. Both fused and crystalline quartz are chemically inert and heat resistant and, therefore, have been much used in laboratory equipment; the additional property of admitting ultra-violet rays makes quartz useful for optical instruments and sun lamps.

A little-known property of quartz, piezoelectricity, observed as early as 1880 by the Curie brothers (*1*), became very valuable in World War II in the field of fixed frequency communication. The natural supply was so depleted that shortly after the war a rather concentrated investigation into the possibility of making piezoelectric quartz crystals artificially was initiated.

The asymmetry of quartz crystals is caused by the spiral arrangement of the silicon-oxygen linkages in the crystals. When the asymmetry is pure (only one spiral direction present) the crystal possesses piezoelectric properties; when the crystal contains both right-handed and left-handed asymmetry, it has a twinned structure which eliminates its piezoelectric qualities.

The phenomena of piezoelectricity, the electric charge developed by asymmetric crystals when pressure is applied, had been observed by earlier workers (*2*) but the Curies were the first to measure the charge and find it to be proportional to the stress applied. The converse effect, the production of strain in the crystal when voltage is applied, was predicted by Lippmann (*3*) in 1881 and later confirmed by the Curies.

The strain produced in an untwinned quartz crystal by applied voltage reverses itself when the polarity of the applied voltage is reversed. When subjected to pulsing or alternating current, the crystal will vibrate. The amplitude and the frequency of the vibration are governed largely by the dimensions of the crystal and by the relationship of the direction of symmetry to the location of the electrodes.

Wafers cut from quartz crystals and carefully ground to predetermined thickness have been used successfully as oscillator controls in many instruments; the greatest application of such quartz wafers has been in the field of fixed frequency communication. The inherent stability of quartz through a wide range of temperature changes and climatic exposure means that the wafers will retain their piezoelectric properties under extreme conditions. The versatile application and theoretical explanation of quartz crystals can be found in a number of references (*4–8*).

The availability of good untwinned quartz for this purpose has been a most pressing problem since most of the natural source has been from the state of Minas Gerais, Brazil. Even this source is limited because the supply is not found in concentrated masses but scattered throughout the area. The demand for fixed frequency communication in World War II depleted the supply considerably and made imperative the attempt to produce oscillator grade quartz from another source.

In 1851, H. de Senarmont (*9*) found that quartz could be crystallized from silicate solutions at high temperatures and pressures. G. Spezia (*10*) found quartz crystals produced in solutions of sodium silicate under similar conditions in 1905. During World War II, R. Nacken (*11*) further developed the process and produced untwinned quartz by the use of an untwinned seed crystal. Based on this information, several projects for investigating the production of oscillator grade quartz were set up under the auspices of the Signal Corps Engineering Laboratories at Fort Monmouth, New Jersey, in 1946.

The conditions under which SiO_2 becomes sufficiently soluble in water solutions were indicated by the observation of aqueous inclusions found in natural quartz crystals. If we assume that at the time of crystal formation the liquid occupies the full volume, an observation of the void space found after the cell has cooled allows an estimation of the temperature at which the crystal was formed. In this manner, the temperature of crystal formation was estimated to be from 300 to 400°C. Nacken used temperatures in this range for his work.

Two general methods of supplying SiO_2 to the seed crystal under conditions where saturation would cause growth were available. They can be described as the Isothermal System and the Gradient System. The Isothermal System requires constant temperature throughout and as a source SiO_2 in such form that it is more soluble than the seed. Fused quartz as a source

—The cover

The size and quality of synthetic quartz crystals now available are demonstrated by this photograph of a crystal grown by the Electronic Research Division of the Clevite Corporation, Cleveland 8, Ohio. The Editor gratefully acknowledges the cooperation of Dr. Hans H. Jaffe and Mr. Danforth R. Hale of the Clevite Corporation.

fulfills the requirements very well since its energy content is much higher than crystalline quartz. The Gradient System allows almost any type of quartz as a source material since the SiO_2 is maintained at a higher temperature than the seed and hence is more soluble.

The Gradient System has been much more useful than the Isothermal System as a method of growing large crystals. However, the Isothermal System has been more valuable in tracing the progress of the reactions necessary for growing crystals since one variable, temperature, is eliminated. Also, the difference between the starting material and the crystalline product is easily recognized by index of refraction measurements.

Pilot Plant Production of Oscillator-Grade Quartz

In 1946, projects directed toward quantity production of oscillator-grade quartz were started at the Brush Development Company and have since been continued at the Clevite Corporation at Cleveland, Ohio, and the Bell Telephone Laboratories at Murray Hill, New Jersey. The former was under contract to the Signal Engineering Laboratories at Fort Monmouth, New Jersey, and the latter was self-supported at first and later became a Signal Corps contractor.

Both of these projects used the thermal gradient method, which as a rule involved maintaining a supply of quartz in the form of irregular pieces immersed in a solution of Na_2CO_3, NaOH, or a combination of the two. This mass of material was kept at a temperature usually above 300°C in a high pressure container that was filled to about 80% of its volume with solution. In a different part of the system, seed plates or bars of good oscillator-grade quartz were suspended in racks designed in such a manner that a plate could add quartz without interfering with any of the other plates in the rack. The seed plates were maintained at a temperature approximately 20°C lower than the source material.

Since the solution at the source became saturated with SiO_2 at a higher temperature, the seed at the lower temperature was surrounded by a solution that was slightly supersaturated with SiO_2. Careful adjustment of the temperature gradient allowed the growth process to be controlled.

The apparatus first used, in the pilot-plant operation, consisted of a pair of autoclaves connected in such a manner that on tilting the pair the solution could be circulated from the source chamber to the seed chamber. This pilot plant operation was initiated in June, 1953, under Clevite Corporation control as a part of the Industrial Preparedness Studies Program, Signal Corps Contract DA36-039 SC-15371.

The Bell Telephone Laboratories, in cooperation with Western Electric Company, put into operation in 1958 (*12*) a group of four vertical autoclaves in which the source material is placed in the bottom and the seeds in the top. The seeds are separated by baffles from the source and since the bottom is kept at a higher temperature than the top, convection currents directed by the baffles carry the SiO_2 to the seeds. The 80% filling at room temperature insures that the container is full when the temperature of the system is maintained near 400°C. This system operates at pressures nearly 30,000 psi. Diagrams of the two systems are found in Figures 1 and 2. A vertical system similar to that used by the Bell Laboratories is now being used by the Clevite Corporation.

Figure 3 shows finished crystals being removed from a vertical autoclave. The sizes of the crystals are different because seed plates of different size have been used. Figure 4 shows a cluster of synthetic crystals as they were taken from quartz-growing autoclave. Use of "Y-bar seed" permits optimum use of high pressure volume and yields crystal shapes well adapted for being cut into resonater plates.[1] Threaded metal rods and other metal parts supported the seeds and were attached to additional seed-holding supports below this cluster. Length of long crystal at left is $7^1/_3$ in. The seed weighed about 15 g, the grown crystals, 242 g.

Mechanism of Crystal Formation

The mechanisms of quartz solution and crystal growth have been investigated by the author of this paper and co-workers at Antioch College. The work began in 1946 under the direction of Dr. Allyn Swinnerton and was continued after his death in 1952 under the direction of Dr. G. E. Owen and under the direction

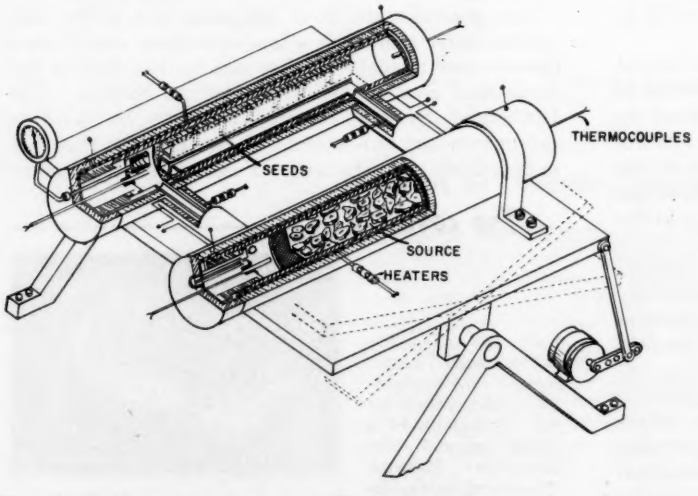

Figure 1. Rocking type autoclave system. (The Clevite Corp.)

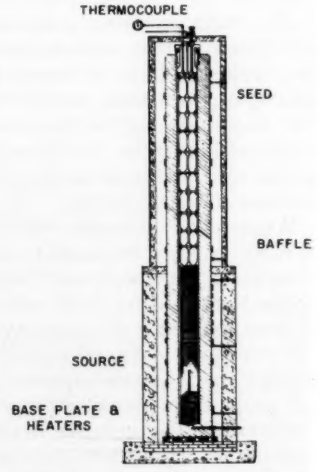

Figure 2. Vertical autoclave system. (Western Electric Company.)

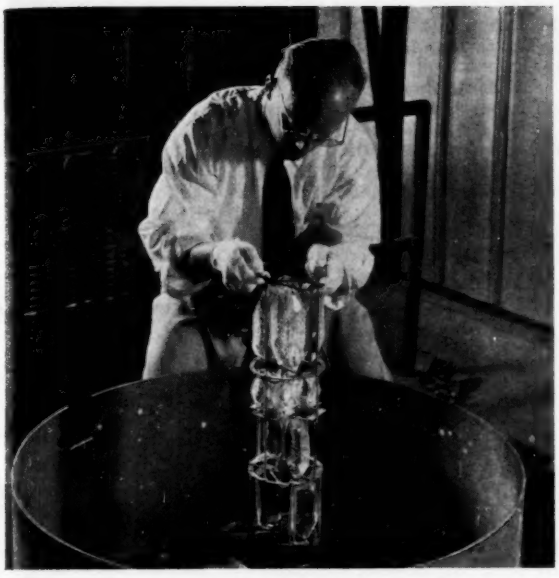

Figure 3. Finished crystals being removed from autoclave. (Bell Telephone Laboratories).

of this author since 1954. The work has been supported by the U. S. Army Signal Corps during the entire time and by the Air Force Office of Scientific Research since 1955.

Since the fact that quartz crystals could be grown from SiO_2 saturated basic solutions at temperatures above 300°C had already been reported by Nacken (*11*), the questions that remained to be answered were *why* and *how*. An interesting facet of the research was the exploration of natural quartz crystal formation.

The transfer of SiO_2 from source to seed is ionic; this was established by Yalman (*13*) by isotopic exchange using H_2O^{18}. Determining the ion that leads to the crystallization of good α-quartz was complicated by the ionization of orthosilicic acid in steps and by the fact that the reaction is highly susceptible to variation in *p*H. Corwin, *et al.*, (*14*) showed that neutral and slightly acid solutions led to the formation of α-cristobalite (symmetrical crystalline form of SiO_2) rather than α-quartz. This result was confirmed by the observation made by Franke (*15*) that when solutions of KOH below 0.0004 *N* were used, a mixture of α-quartz and α-cristobalite was obtained. It was found that under isothermal conditions, the best and fastest α-quartz formation (*16*) was accomplished by maintaining the solution at *p*H 10. Calculation from ionization constants for orthosilicic acid showed that at the optimum *p*H, $H_2SiO_4^{--}$ [or $SiO_2(OH)_2^{--}$] was the ion that was most prevalent by a ratio of 500:1. The sharp change in crystalline form due to the *p*H of the solution was demonstrated by Yalman (*16*) using NaOH solutions.

The application of laboratory conditions to the natural formation of α-quartz led to the examination by Corwin, *et al.*, (*17, 18, 19*) of the effect of alkaline earth metal oxides and compounds on the growth of quartz, and it was found that in the presence of solutions of these salts no α-quartz was formed. Where the alkalinity of the original solution was sufficient for α-quartz formation, the corresponding silicate formed was too insoluble to promote further reaction, and where the silicate was soluble enough, the *p*H was so low that cristobalite was the result.

In nature, α-quartz crystals are found deposited with alkaline earth metal salts like $CaCO_3$. It can only be concluded from laboratory experimentation that during the natural formation of the α-quartz there were sufficient alkali metal salts present to provide the necessary *p*H. Subsequent drainage and leaching of the deposits removed the soluble materials. A review of mineralogical data where crystal structure information is available shows that the presence of cristobalite and opal (a hydrated form of cristobalite) is usually accompanied by acid or neutral clays.

Summary

The investigation of the hydrothermal systems that have developed oscillator-grade α-quartz since World War II has resulted in the development of pilot plants for commercial production by artificial means of quartz crystals similar to those found in nature. As a by-product of this investigation an insight has been gained into the actual mechanism of quartz formation and some conclusions have been drawn concerning the natural processes.

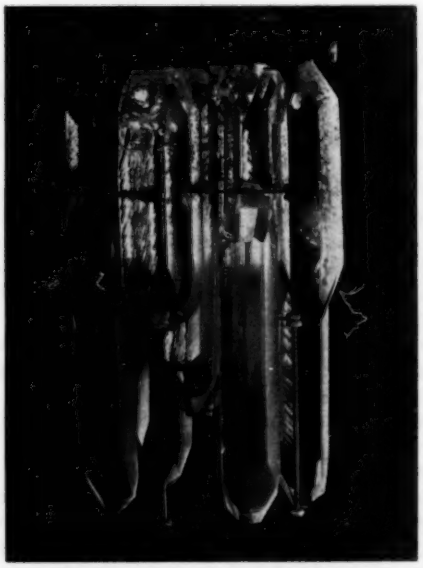

Figure 4. Crystals grown from "Y-bar Seeds." (Electronic Research Division, Clevite Corporation.)

[1] Data on the relative costs of cultured quartz in comparison with natural for standard oscillator plates 0.400″ square by 0.035″ thickness was received by the author from Dr. C. B. Sawyer, of the Sawyer Research Products Co., Eastlake, Ohio, in a private communication. The first sale of cultured quartz was made by the Clevite Corporation in May, 1955, at $52.50 per pound. The latest price was established by the Sawyer Research Products Co. in July, 1958, at $27.50 per pound. This price in comparison with natural quartz is 23% cheaper due to the ability to furnish cultured quartz crystals which have the shape that can be cut efficiently. The data below show the advantage.

Cultured Quartz: $27.50 per pound
Yield: 670 oscillator plate blanks per pound from cultured quartz.
84 blanks per pound from natural quartz.
Cost of Material: Cultured quartz 17% greater than natural.
Labor cost: 41% less for cultured quartz.
Over-all cost: 23% less than for natural quartz.

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The Hydration of Carbon Dioxide

The neutralization of carbon dioxide is a slow process compared with that of other weak acids. This can be shown by a simple experiment. Two 70-ml portions of 0.01 *M* NaOH are colored with phenolphthalein. A slight excess of acetic acid is added to one, and an equal number of moles of carbonic acid (25 ml of saturated CO_2 solution) to the other. The first portion loses color as fast as the solutions can be mixed. No immediate change takes place in the carbonic acid mixture; then a slow fading sets in which is complete in about fifteen seconds.

The reason for the delay is that only a small fraction of aqueous CO_2 exists in the hydrated form H_2CO_3. The slowness of the interconversion carbon dioxide$\rightleftharpoons$ hydrated carbonate species is of great importance in industrial, analytical, and biological chemistry. Its kinetics have been examined over a long period and by a wide variety of techniques. It acquires additional interest from being one of the first "rapid" equilibria ($t_{1/2} < 1$ sec) to be quantitatively studied. This article traces the work on CO_2 kinetics from its crude beginnings to the most recent (1958) measurements. Experimental precision has progressed so far that the system is sometimes used as a standard for testing new kinetic measuring devices. There are, however, still unresolved differences in the reported equilibrium constants.

To help the reader appreciate the problems faced by early workers, the modern conception of the reaction mechanism is summarized below. The constants are for 25°; they have been adjusted where necessary to insure internal consistency.

Neutralization of CO_2 can occur by two paths. At pH <8 the predominant mechanism is via direct hydration:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1)$$

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O \text{ (instantaneous)} \quad (2)$$

The rate law is pseudo first order:

$$-d(CO_2)/dt = k_{CO_2}(CO_2),\ k_{CO_2} = 0.03\ \text{sec}^{-1} \quad (3)$$

At pH > 10, direct reaction with OH^- predominates:

$$CO_2 + OH^- \rightarrow HCO_3^- \quad (4)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{--} + H_2O \text{ (instantaneous)} \quad (5)$$

with the rate law:

$$-d(CO_2)/dt = k_{OH}(OH^-)(CO_2),\ k_{OH} = 8500\ \text{sec}^{-1}\ (\text{mol/l})^{-1} \quad (6)$$

This rate law can also be interpreted simply as a basic catalysis of reaction (1). The two concepts are experimentally indistinguishable. In the pH 8–10 range, both mechanisms are important. Reactions (1) and (4) are referred to as hydration processes. To each there corresponds a dehydration process:

$$H_2CO_3 \rightarrow H_2O + CO_2,\ k_{H_2CO_3} = k_{CO_2} \times K = 20\ \text{sec}^{-1} \quad (7)$$

$$HCO_3^- \rightarrow OH^- + CO_2,\ k_{HCO_3^-} = k_{OH} \times KK_w/K_a = 2 \times 10^{-4}\ \text{sec}^{-1} \quad (8)$$

For the equilibrium: $H_2CO_3 \rightleftharpoons CO_2 + H_2O$,

$$K = (CO_2)/(H_2CO_3) = k_{H_2CO_3}/k_{CO_2} = ca.\ 600 \quad (9)$$

A consequence of equilibrium (9) is that the true ionization constant of H_2CO_3,

$$K_a = (H^+)(HCO_3^-)/(H_2CO_3)$$

must be much greater than the apparent constant listed as K_1 for carbonic acid in tables of acid dissociation constants,

$$K_1 = (H^+)(HCO_3^-)/(CO_2 + H_2CO_3) = 4.45 \times 10^{-7},$$

for the observed ionization originates from only a small fraction of the total carbon dioxide content. It is easily shown that

$$K_a = K_1(1 + K) = ca.\ 2.5 \times 10^{-4} \qquad (10)$$

The Early Period: Conventional Colorimetric and Conductometric Methods

Although the base-neutralizing powers of CO_2 had been known and exploited since before 1800, the slowness of the reaction went unnoticed until 1912. In that year the Englishman McBain (*1*) found that the fading phenolphthalein end point commonly observed when acid is titrated with base was not caused by slow absorption of CO_2 from the air, as generally supposed. Instead, the carbonate impurity in the base was responsible. The carbonic acid which accumulated in the solution during the titration had ample time to change to CO_2 and in this form reacted relatively slowly with the base, causing premature, impermanent end points.

The slow reaction was discovered independently the next year by Vorländer and Strube (*2*). They observed fading phenolphthalein end points when they attempted to titrate CO_2 solutions with $Ca(OH)_2$ and $Ba(OH)_2$. Their crude measurement of color fading times in mixtures of base and excess CO_2 produced the first kinetic data, but they made no attempt to work up their figures. The results were in any case needlessly obscured by the precipitation of insoluble carbonates. Like McBain, they postulated a slow hydration; but they suggested that the gas was actually present as bubbles of colloidal dimensions, implying that physical solution rather than chemical transformation was the slow step.

Their work was criticized in a note by Thiel (*3*), an aggressive physical chemist who had already embarked on an investigation of his own. The problems to which he addressed himself were (*a*) the equilibrium concentration of H_2CO_3 in a CO_2 solution, and (*b*) the rate and mechanism of CO_2 neutralization. There were already grounds for believing the equilibrium (H_2CO_3) to be small. Although H_2CO_3 was the form usually written for dissolved CO_2, a comparison of the structure of H_2CO_3 with that of simple organic acids had led several authors to predict a much higher ionization for this acid than was actually observed in CO_2 solutions. The possibility that such solutions contained only a small quantity of highly ionized H_2CO_3 had been explicitly suggested.[1] But it was assumed that as with NH_3 and SO_2, the CO_2 hydration rate was immeasurably fast.

Thiel's method (*4*) for determining the equilibrium (H_2CO_3) was to measure how much base a solution of CO_2 would neutralize instantaneously, before there was time for more H_2CO_3 to form. Clearly the success of the experiment depended on rapid mixing of the reactants. The mixer consisted of a small beaker cemented to the bottom of a stoppered cylinder which was shaken by hand. After much practice with equivalent quantities of strong acids and bases placed separately in the beaker and the annular space, Thiel claimed complete mixing (as shown by disappearance of the phenolphthalein color) within 0.4 sec. The operation was then repeated with increasing concentrations of NH_3 or NaOH and a fixed concentration of CO_2 until the red color persisted longer than 0.4 sec. It turned out that about twice as much NaOH was required as NH_3. Thiel correctly interpreted this as proving that the more basic reagent speeded up CO_2 hydration so that more than the equilibrium H_2CO_3 concentration was being neutralized. Hence the NH_3 results were more reliable. In this way Thiel was led to propose the hydroxide mechanism (4) in basic solution, for mechanism (1) would have led to equal neutralization rates with all bases.

In the calculation of (H_2CO_3), allowance had to be made for the fact that both unionized and ionized H_2CO_3 are measured by this technique. Because of the considerable strength of H_2CO_3 and its low concentration, it was in fact almost 90% dissociated in Thiel's solutions. To find (H_2CO_3), he subtracted from his data the concentration of HCO_3^-, as calculated from the then accepted value of K_1. Considering that (H_2CO_3) was obtained as a small difference between two large numbers, one derived from an inherently inaccurate experiment and the other from an equilibrium constant (K_1) notoriously difficult to measure, Thiel's result, $K_a = 1.9 \times 10^{-4}$ at 4°, was remarkably accurate.[2]

He was less fortunate in his kinetic experiments (*5*). Since he knew of no rapid means of determining dissolved CO_2 as distinct from the hydrated form, he fell back upon a *p*H-measuring technique elaborated from the method of Vorländer and Strube. Sodium hydroxide solutions were mixed manually with a slight excess of CO_2, and the time required to reach successive *p*H values in the 9–7 region was determined colorimetrically by subjective matching against appropriate buffer standards.

The principle of this method is sound, and it was used successfully in subsequent work. But the relationship between *p*H and time in such experiments is very involved. When equimolar quantities of CO_2 and OH^- are mixed, almost all the OH^- and half the CO_2 first react rapidly to form $CO_3^=$ (reactions (4) and (5)). The remainder of the neutralization is best expressed by the net equation

$$CO_3^= + CO_2 + H_2O \rightarrow 2HCO_3^- \qquad (11)$$

which occurs in a carbonate-bicarbonate buffer of slowly diminishing *p*H. In this stage the (OH^-) is very low but is continually regenerated by hydrolysis of the $CO_3^=$. What is more, as the *p*H drops below 10, the rate of the OH^- mechanism diminishes to the point where the direct hydration mechanism offers serious competition. It was precisely in this range that Thiel made his experimental observations, since the rate at higher *p*H was too rapid for him to follow. Unfortunately, Thiel overlooked the existence both of the competing mechanism and the carbonate-bicarbonate buffer. For him the equation $OH^- + CO_2 = HCO_3^-$ was a complete description of the process, with no intermediate $CO_3^=$ formation.

Naturally the simple second order law which such a conception demands did not fit his data. In order to

[1] See (*9*) for the early literature.

[2] This value has been corrected as suggested by Faurholt (*12*).

accommodate the apparent retarding effect of the HCO_3^- product, actually caused by its neutralization of OH^- and its role as an acid buffer constituent, he was forced to introduce it as an arbitrary inverse term in his purely empirical rate law:

$$-d(CO_2)/dt = k(CO_2)(OH^-)/(HCO_3^-).$$

At this point Thiel's work was interrupted by the First World War. The problem was thereafter taken up by Pusch (*6*) under the (no doubt distant) guidance of Nernst and Eucken. In a new approach, the course of the CO_2-OH^- reaction was followed conductometrically. Unfortunately Pusch borrowed her concept of the reaction from Thiel and remorselessly pursued to its logical conclusion his literal interpretation of equation (4). The change in conductivity as the reaction proceeded was attributed exclusively to the conversion of OH^- to HCO_3^- and hence was taken as a direct measure of the reaction's progress although this involved the untenable assumption that large amounts of OH^- and HCO_3^- existed together in the same solution. (Because of its high speed, she observed only the last 5% of the conductivity change, which was actually due to reaction (11)). While her confirmation of Thiel's rate law did not represent a useful advance, the introduction of conductometry proved fruitful in the hands of later workers.

Pusch was the first to investigate the hydration kinetics in acid solution. She sought evidence for the slow reaction $CO_2 + H_2O \rightarrow H_2CO_3$ by observing the conductivity of a pure CO_2 solution after sudden dilution. The slow hydration of CO_2 might be expected partially to delay the increased ionization characteristic of a diluted acid. Considering the time-consuming dilution method adopted, it is not surprising that this short-lived effect could not be observed. Pusch inferred from her experiment a very rapid direct hydration. She reconciled this with her views on the mechanism in basic solution by assuming acid catalysis.

Pusch's work drew a reply[3] from Thiel (*7*) in which he asserted a claim to mental priority with regard to the conductivity method and requested that the CO_2 problem be respected as his private research territory. He then drew attention to the recent paper of his pupil Strohecker (*8*) which rejected the incorrect HCO_3^- mechanism on which Pusch's work had been founded. But even with this theoretical improvement, the experimental inaccuracy inherent in Thiel's method prevented further progress, quantitative or qualitative. The final conclusions of Strohecker, as before, were that the hydroxide mechanism (*4*) predominated in basic solutions, and an acid catalyzed direct hydration in acid solution.

Later German contributions were curious rather than helpful. Wilke (*9*) in 1921 presented reasons for supposing that $C(OH)_4$ was the predominant species in carbon dioxide solutions, the absence of a carbonyl oxygen accounting for the low acidity. His rather vulnerable arguments were demolished (*10*) by the ever-watchful Thiel (who never returned to work his claim).

A curious anachronism is presented by a late paper of Eucken and Grutzner (*11*). Unaware of Faurholt's definitive study three years earlier, Eucken sought to improve on the work of his former pupil Pusch. Using a more effective mixing procedure, he succeeded in detecting qualitatively the brief increase in conductivity subsequent to dilution of a CO_2 solution. Eucken attempted to reinterpret the previous work of Pusch and Strohecker in the *p*H 7–10 range on the assumption that direct hydration was faster than had been supposed and was the only effective mechanism up to *p*H 10. It is a poor tribute to the available experimental data that they actually conformed rather well to this conception; but the first order rate constant which his mathematical treatment yielded him was of course far too large, since it was actually a composite of k_{CO_2} and k_{OH} (OH^-).

Eucken tackled the hydration rate in pure carbon dioxide solutions by an original method based on the selective reduction of H_2CO_3 at a rotating micro-electrode. Specialists in polarographic kinetics will be surprised to find in this paper a theory of kinetic waves which is universally believed to be a post-war development. Unluckily the CO_2 system to which he applied his theory did not in fact satisfy certain assumed conditions so that his derivation of a rate constant which agreed well with the one he had found in more basic solution must be considered fortuitous. It is unfortunate that a theory well in advance of its time should have been used only to support an outdated reaction scheme and then allowed to sink into neglect.

Eucken's work did not of course escape the notice of Thiel. In a note added in proof, Eucken thanks his colleague for drawing to his attention the work of Faurholt, whose results did not appear to be in accord with his own.

The Carbamino Quenching Method (1924)

Faurholt (*12*) made his elegant and comprehensive study of CO_2 kinetics while acting as Niels Bjerrum's assistant at the Royal Institute of Veterinary Medicine and Agronomy in Copenhagen. His painstaking experiments required no more elaborate apparatus than a flask and filter funnel, yet his values for the rate and equilibrium constants of the CO_2-H_2CO_3 system, at least at O°, have hardly been improved upon by later work.

Crucial to his method was the fact (*13*) that alkyl amines (in particular dimethyl amine) react extremely rapidly with unhydrated CO_2 to form carbamates

$$CO_2 + 2R_2NH \rightarrow (R_2NCO_2^-)(NH_2R_2^+)$$

At the same time the amine neutralizes H_2CO_3, converting it to HCO_3^-, and CO_3^{--}. A reaction involving the interconversion $CO_2 \rightleftharpoons H_2CO_3$ is therefore instantly quenched in both directions. The method in brief was to mix a CO_2 or carbonate solution (for the forward and reverse reactions respectively) with a buffer of known *p*H, and follow with a large excess of 4 *M* amine after the desired reaction time had elapsed. $BaCl_2$ was used to precipitate the carbonate fraction, leaving carbamate in solution. On being heated, this in turn gradually changed to carbonate and precipitated as the barium salt. The analysis consisted simply of carbonate titrations. In this way the concentrations of hydrated and unhydrated CO_2 could be determined at any instant during the reaction.

[3] Dated "In the field" (Im Felde) where he had just won the iron cross first class, *Z. Elekt.*, **22**, 468 (1916).

Not only were Faurholt's data precise and objective compared with the earlier pH method, but also easier to interpret since the CO_2 concentration itself was measured as a function of time, while the pH was held constant by the use of buffers. Actually there was usually a small change of pH which could be corrected for by approximate methods. The chief source of error lay in the mixing, which he accomplished by pouring the contents of one flask into another, with shaking. Nevertheless the starting and quenching were sufficiently abrupt so that he could work confidently with five- and ten-second reaction times.

Faurholt measured the CO_2 hydration rate in carbonate-bicarbonate buffers of pH 10.3–10.8[4] and phosphate buffers of pH 6–8. This happy choice confined him to regions in which only one mechanism was important. Thus he was the first to unsnarl the competing OH^- and H_2O mechanisms and firmly establish their rate laws (equations (3) and (6)). He found k_{CO_2} to be independent of pH, contrary to the earlier evidence for acid catalysis. The relative slowness of the simple hydration allowed him to follow its course over several minutes (at 0°), compared to the ten seconds available to him during the OH^- reaction in basic buffers. His accuracy can be judged from Figures 1 and 2.

Faurholt broke new ground with his measurement of the dehydration rate constant $k_{H_2CO_3}$ from experiments with carbonate-acid buffer mixtures:

$$2H^+ + CO_3^{--} \rightleftharpoons H_2CO_3 \rightarrow CO_2 + H_2O$$

A difficulty here was that his analytical method did not yield (H_2CO_3), but only the total carbonate whether in the form H_2CO_3, HCO_3^-, or CO_3^{--}. If he used HCl solutions, to be sure, all the carbonate existed as H_2CO_3; the rate was consequently so fast that he had to cope with reaction times of only one second. Above pH 3 the rate was more manageable because of the smaller H_2CO_3 fraction:

$$d(CO_2)/dt = k_{H_2CO_3}(H_2CO_3) = \alpha k_{H_2CO_3}\text{ (total carbonate), where} \quad (12)$$

$$\alpha = (H_2CO_3)/(\text{total carbonate}) = (H^+)/[(H^+) + K_a] \quad (13)$$

αk_{HCO_3} is the "practical" constant obtained directly from the (total carbonate)-time data. To find α one needs the true ionization constant K_a. In Faurholt's time there was only Thiel's questionable figure. In principle both $k_{H_2CO_3}$ and K_a should be calculable from a series of $\alpha k_{H_2CO_3}$ determinations in buffers of pH 3–6, but Faurholt's rather imprecise data were able to accommodate a disconcerting range of values for the two constants. The upshot was that he relied mainly on the fast strong acid measurements (See Table 2).

Now that the simple hydration had been examined from both directions, several roads lay open to the calculation of K_a or the CO_2-H_2CO_3 constant K (related by equation (10)):

(1) From the rate constants, $K = k_{H_2CO_3}/k_{CO_2}$;
(2) By direct measurement of the equilibrium carbonate in CO_2 solutions, following Thiel but using the quenching rather than the rapid titration method;
(3) By combining $\alpha k_{H_2CO_3}$ measured at pH > 3 with $k_{H_2CO_3}$ found in strong acid. (This yields K_a through equation (13)).

The values agreed within ±50%. Faurholt preferred $K = 900$ and $K_a = 2 \times 10^{-4}$ at 0°.

Once K, K_1, and K_a are known, the equilibrium concentrations of CO_2 and the various carbonate species can be calculated for any pH. Table 1, originally given by Faurholt, has been recalculated on the basis of the constants given at the beginning of the article. The value $K_2 = 4.8 \times 10^{-11}$ was used for the second dissociation constant of carbonic acid (25°).

Table I. Rate Constants, Half Life and Equilibrium (CO_2) for the Carbon Dioxide-Carbonate Equilibrium in Aqueous Solution (25°)

pH	% CO_2	k_{CO_2}	$k_{OH}(OH^-)$	$\alpha k_{H_2CO_3}$	$\alpha' k_{HCO_3^-} \times 10^4$	$t_{1/2}$[a] (sec)	$t_{1/2}$[b] at 0° (sec)
1	99.8	0.03	0.0000	20	0.005	0.05	0.38
2	99.8	0.03	0.0000	20	0.05	0.05	0.39
3	99.8	0.03	0.0000	16	0.38	0.06	0.48
4	99.4	0.03	0.0000	5.7	1.4	0.18	1.33
5	96.0	0.03	0.0000	0.77	1.8	1.25	9.7
6	70.6	0.03	0.0001	0.080	1.9	9.1	74
7	19.3	0.03	0.0008	0.008	1.9	26.0	240
8	2.3	0.03	0.0085	0.001	1.9	25.0	300
9	0.2	0.03	0.085	0.000	1.8	8.7	200
10	0.0	0.03	0.85	0.000	1.3	1.14	47
11	0.0	0.03	8.5	0.000	0.33	0.12	5.4
12	0.0	0.03	85.0	0.000	0.038	0.012	0.53
13	0.0	0.03	850.0	0.000	0.004	0.0012	0.053
14	0.0	0.03	8500.0	0.000	0.000	0.0001	0.0053

[a] The half time to attain equilibrium is given by $t_{1/2} = \frac{\ln 2}{\Sigma k_{CO_2} + \Sigma k_{carb}}$ in which $\Sigma k_{CO_2} = k_{CO_2} + k_{OH}(OH^-)$ and $\Sigma k_{carb} = \alpha k_{H_2CO_3} + \alpha' k_{HCO_3^-}$. The α terms represent the fraction of total carbonate present as H_2CO_3 and HCO_3^- respectively.

[b] The shift of the maximum half time toward higher pH at 0° is caused primarily by the change in K_w: pOH + pH = 14.96 at 0°. This especially influences the figures for $k_{OH}(OH^-)$.

The figures show that from pH 5–8 neither hydration nor dehydration is complete. If accurate values of k_{CO_2} and $k_{H_2CO_3}$ are sought in near neutral solution, it follows either that allowance must be made for the back reaction or that only the initial stage of the reaction should be measured. In fact Faurholt, in evaluating his CO_2 hydration experiments in this range, applied the well-known equation for a reversible first order reaction:

$$CO_2 \underset{\alpha k_{H_2CO_3}}{\overset{k_{CO_2}}{\rightleftharpoons}} \text{carbonate}, \quad K_\alpha = \frac{k_{CO_2}}{\alpha k_{H_2CO_3}}$$

$$[k_{CO_2} + \alpha k_{H_2CO_3}]t = \ln \frac{(CO_2)_0 K_\alpha}{(CO_2)_0 K_\alpha - (CO_2)_t[1 + K_\alpha]}$$

The Rapid Flow and Manometric Methods (1928–1938)

Now that the ground work was laid, carbon dioxide kinetics entered its most flourishing period, spurred on by two developments, a mass invasion of the field by the biochemists, and the discovery of a general method for measuring rates with half times down to 0.001 sec.

Hartridge and Roughton (*15*), working at Cambridge, invented the widely used rapid flow technique in 1923. Reactant solutions were forced at high speed through multiple jets into a small mixing chamber and thence up a glass observation tube. Mixing was complete within a few milliseconds. The distance traveled up the tube was proportional to the time elapsed after mixing. One could therefore have any stage of a rapid reaction under continuous observation by choosing the appropriate point along the tube. Hartridge and Roughton first applied their technique to the oxygen-hemoglobin reaction, measuring its progress spectroscopically. In 1925 they suggested the need for

[4] Extended to a higher pH in an earlier paper (*14*).

studying the $HCO_3^- \rightleftharpoons CO_2$ equilibrium in the blood.

The first rapid flow data were secured by Saal (*16*) in Holland. He followed the fast reaction, $2OH^- + CO_2 = CO_3^{=} + H_2O$ (equations (4) and (5)) in NaOH $-CO_2$ mixtures, over a period of 1.7 sec. The replacement rate of OH^- by CO_3^{--} was measured conductometrically, with the aid of pairs of platinum wires sealed at intervals into the observation tube. At the same time Saal made the first "direct" measurement of K_a. Bringing together approximately equivalent amounts of H^+ and HCO_3^- in the mixing chamber, he was able to measure the conductivity of his H_2CO_3 solution before any considerable dehydration to CO_2 had taken place. He had thus snatched from his reacting system the data from which weak acid constants are normally calculated under placid equilibrium conditions. He found $K_a = 3 \times 10^{-4}$ (13.5°).

The conductivity of the H_2CO_3 solutions fell off at more distant points as dehydration proceeded:

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightarrow CO_2 + H_2O$$

These additional data yielded a rather uncertain $k_{H_2CO_3}$. An independent, reasonably concordant value was secured by measuring instead the decline in the hydrogen ion concentration. This Saal accomplished by platinizing the electrodes, saturating the reacting solutions with H_2, and placing a reference electrode in contact with the outflow. His detailed description of difficulties arising from poisoning and potential drift effectively discouraged further use of the H_2 electrode in flow systems, though Dirken and Mook (*17*) employed quinhydrone and antimony electrodes in 1930. The potentiometric *p*H method was also applied to static systems, with varying success.[5] The work of Stadie and O'Brien (*18*) is an example of the latter technique. They used the quinhydrone electrode and photographed the deflection of a galvanometer as it moved under the influence of the *p*H changes caused by hydration or dehydration of CO_2. Initial mixing was performed by adjusting the densities of the reacting solutions with sugar, floating one upon the other, and suddenly agitating with a mechanical stirrer.

About this time (1928) some experiments of Henriques (*19*), working at Copenhagen, brought the biochemists into the field in full cry. The CO_2 produced by the body cells is carried off by the blood (*p*H = 7.4) primarily as HCO_3^- and is eliminated in its brief passage through the lung capillaries. A simple calculation based on Faurholt's figures showed that the normal H_2CO_3 dehydration rate, even at blood temperature, was far too slow to account for the observed CO_2 evolution. Direct measurements of the rate of CO_2 elimination from blood, initiated by Henriques and elaborated by other workers, revealed a pronounced catalysis. The catalytic agent was soon isolated in concentrated form as the enzyme carbonic anhydrase which is found in the blood corpuscle and is so potent that one part in 10^7 doubles the dehydration rate. Since then an unbroken series of papers have concerned themselves with the chemistry and physiology of this catalysis (*20*, *21*). This interest also did much to stimulate measurements of the uncatalyzed reaction, in particular by the biochemist Roughton and his co-workers, who have continued their investigations to the present day.

The first major investigation, by Brinkman, Margaria, and Roughton (*22*), was undertaken to improve upon Faurholt's accuracy and at the same time to decide once and for all whether the simple hydration reaction was acid catalyzed, a question which recent experimental work had revived. These authors adopted an elementary yet powerful manometric technique that had been originated by Henriques but could just as well have been used by the earliest German workers.

To measure k_{CO_2}, they shook basic buffers in a CO_2 atmosphere in a thermostated vessel connected to a manometer. The concentration of dissolved unhydrated CO_2 was assumed to be proportional at all times to the observed partial pressure of CO_2 gas. The reverse rate was determined from CO_2 evolution experiments with bicarbonate-acid buffer mixtures. Since the establishment of equilibrium between gaseous and aqueous CO_2 was far from instantaneous, even with vigorous mechanical agitation, the technique was restricted to reactions of half life greater than 45 sec. From Table 1, it follows that the method is applicable to the *p*H range 6–10. For hydration (CO_2 absorption) the range is somewhat extended because the gaseous phase, acting as a reservoir of reactant, maintains the level of dissolved CO_2 and lengthens the effective half life. Hydration rates could therefore be measured even at *p*H 11, to yield values for k_{OH}.

The treatment of the data was similar to Faurholt's since in both cases the CO_2 concentration was the measured variable. However, $k_{H_2CO_3}$ could not be measured directly in strongly acid solutions as Faurholt did because the reaction was too fast. What Brinkman measured in his near neutral buffers was really the rate of the reaction

$$H^+ + HCO_3^- \xrightarrow{k} CO_2 + H_2O$$

for the H_2CO_3 intermediate in equilibrium with HCO_3^- was present at very low concentration. Comparison with equations (12) and (13) shows that at low acidities,

$$k = \alpha k_{H_2CO_3}/(H^+) = k_{H_2CO_3}/K_a$$

To calculate $k_{H_2CO_3}$ the authors accepted Faurholt's value for K_a. They avoided the back reaction correction by keeping to the initial stages only.

The results by the manometric method confirmed Faurholt's mechanisms; the quantitative agreement was not so good.[6] As some kind of interference might have been created by the presence of a phase boundary in the manometric method, Brinkman, *et al.*, checked their results by their photoelectric rapid flow technique. Solutions of HCO_3^- or CO_2 were mixed with solutions of appropriate *p*H and examined at various distances from the mixing chamber with the aid of a photoelectric cell. An acid-base indicator provided the variation in optical density. The rate at which H_2CO_3 entered or left the weakly or unbuffered systems was estimated from the rate of *p*H change. All three rate constants were measured in this fashion. The two sets of data were fairly concordant, but at this stage in their development neither method was in fact very

[5] See (*22*) for a discussion of this work.

[6] It was later pointed out (*18*) that this was mostly caused by Faurholt's having omitted the treacherous logarithmic factor 2.3 from all his rate constant calculations. This error has been corrected in the data quoted in this article.

accurate. Being a high speed technique, the photoelectric method had the advantage of permitting direct measurement of the dehydration rate in HCl-HCO_3^- mixtures with results more reliable than those of Faurholt. In this, as in several other repects, the photoelectric experiments resembled the work of Saal.

During later manometric experiments (*23*) Roughton and Booth (1938) made the unsettling discovery that the $H_2O + CO_2 \rightleftharpoons H_2CO_3$ equilibrium (but not the basic mechanism) was base catalyzed and hence influenced by the basic constituents of the buffers used in past work. Fortunately the catalysis was easily corrected for by a linear extrapolation to zero buffer concentration. The result was to lower the most probable values of k_{CO_2} and $k_{H_2CO_3}$ by 20%. Reevaluation of the old data showed that some of the discrepancies between them could be attributed to this source.

Neither CO_3^{--} or HCO_3^- were catalysts. Certain oxy-anions, especially arsenite, had catalytic effects hundreds of times greater than normal. Br_2 and Cl_2 were later added to this group (*24*). Their mode of operation still remains in the dark, as does also that of carbonic anhydrase, which on a weight basis is over a thousand times more effective than the best of the inorganic catalysts.

The Thermometric Method

The values for $k_{H_2CO_3}$ obtained by direct measurement in HCl-HCO_3^- mixtures had of course never been subject to the buffer error, but they were considered unreliable because of the great speed of the reaction. The early rapid flow measurements of Saal (conductometric and H_2 electrode) and Brinkman (colorimetric *p*H) have been mentioned. Roughton (*25*) returned to the problem armed with a new instrumental weapon. By means of a movable thermocouple junction inserted into the observation tube of the rapid flow apparatus, the course of the reaction was followed as a function of the temperature change in the essentially adiabatic system. This method had been under development by Roughton since 1924 (*26*) and had been applied to the study of CO_2 kinetics in a preliminary way off and on throughout the thirties (*27*).

Roughton's most detailed study (1941) was carried out with a much improved apparatus, capable of following total heat effects of only 0.01° with a 1–2% accuracy over a reaction time of 0.05 sec. The mixing of HCl and $NaHCO_3$ solutions was accompanied by an instantaneous rise in temperature caused by the association

$$H^+ + HCO_3^- \rightarrow H_2CO_3 \qquad (14)$$

A slow temperature rise followed, corresponding to dehydration:

$$H_2CO_3 \rightarrow H_2O + CO_2 \qquad (15)$$

Since the second temperature increase was directly proportional to CO_2 produced, a simple first order treatment sufficed to yield values of $k_{H_2CO_3}$ of an estimated ±5% accuracy.

At the same time the observed temperature rises furnished the first ΔH values for the individual steps, as distinguished from the total heat measurable by classical calorimetry. These data were used to determine the temperature dependence of K_a. From recent manometric measurements of CO_2 evolution from weakly acid buffers (corrected for catalysis) Roughton had an accurate value for $k_{H_2CO_3}/K_a$. Combination of this with his directly measured $k_{H_2CO_3}$ yielded $K_a = 2.5 \times 10^{-4}$ at 0°. The variation of K_a with temperature was calculable from the ΔH data by means of the van't Hoff reaction isobar. The dissociation appeared to increase only slightly as the temperature varied from 0° to 38°. In this same range $k_{H_2CO_3}$ increased eighty fold. The careful measurement of temperature dependence was typical of most later work. Previously data were gathered at one or two temperatures chosen arbitrarily by individual investigators; in the absence of a reliable temperature coefficient, comparison was difficult.

The Isotopic Exchange Method

One of the most important contributions to CO_2 kinetics was made about this time by Mills and Urey (*28*) with their experiments on isotopic exchange between CO_2^{14} and H_2O^8. This exchange occurs exclusively through the hydration equilibrium; its study by these authors produced the only accurate value for the hydration rate k_{CO_2} obtained to date in strongly acid solutions.

In these solutions the chemical equilibrium $H_2O + CO_2 \rightleftharpoons H_2CO_3$ is established in a fraction of a second ($t_{1/2} = 0.69/[k_{CO_2} + k_{H_2CO_3}]$). If CO_2 enriched with heavy oxygen is used, the forward and backward reactions must occur many times before O^{18} is equally distributed between CO_2 and H_2O; therefore the half life for isotopic equilibrium is much longer, in fact about 1000 sec at 0°.

Consider the reaction $CO_2^{18} + H_2O^{16} \rightleftharpoons H_2CO_2^{18}\,O^{16}$ after chemical equilibrium has been reached. The (H_2CO_3) is very small and continually renewed. Its degree of O^{18} enrichment will reflect the momentary composition of the CO_2 and H_2O from which it has just been formed; it will in fact be $^2/_3$ that of the CO_2, since one third of its oxygen derives form H_2O^{16}, which is present in large excess and retains its normal composition throughout the reaction. For each CO_2 molecule that is hydrated in the equilibrium mixture, another is formed by dehydration, with an O^{18} content $^2/_3$ as great. The rate constant for O^{18} impoverishment is accordingly one third that for the forward reaction and has $t_{1/2} = 0.69 \times 3/k_{CO_2}$. This long half life permitted Mills and Urey to use normal techniques of isotopic analysis. After rapid shaking of water with enriched CO_2, samples of CO_2 solution were removed at intervals and vacuum-stripped. The evolved CO_2 was immediately freeze-dried and analyzed in the mass spectroscope. The method is free from all problems of ionic strength, phase boundaries, and indicator corrections. The authors obtained excellent results (Fig. 1) with an original O^{18} enrichment factor of only 2.5. The isotopic half life was greatly extended in further experiments by adding enriched HCO_3^-, but the calculations are too complex to be considered here.

Postwar Electicism and the Stopped Flow Method

Since the war, progress in CO_2 kinetics has been along

the lines of experimental refinement, careful attention to variables such as temperature and ionic strength, and a prolific diversification of technique. An accuracy of ±5% has been quite generally claimed.

Dehydration: $H_2CO_3 \xrightarrow{k} H_2O + CO_2$

All recent experiments on this rapid reaction have involved the observation of *p*H changes in mixtures of HCl with excess $NaHCO_3$. The equilibrium with H_2CO_3 (equation (14)) is established instantly, so that

$$(H^+) = (H_2CO_3) \times \frac{K_a}{(HCO_3^-)}$$

throughout the dehydration reaction (equation (15)). If enough HCO_3^- is present, H_2CO_3 dissociation is almost completely suppressed, and the excess (HCO_2^-) can be treated as a constant. Hence (H^+) is proportional to (H_2CO_3), and we have

$$k_{H_2CO_3}t = \ln (H_2CO_3)_0/(H_2CO_3)_t = \ln (H^+)_0/(H^+)_t$$

which accounts for the observed linear *p*H-time plots. This, in somewhat simplified form, is the treatment accorded their data by all the users of this method, beginning with Saal and Brinkman.

Kinetic studies of this reaction require rapid mixing; if an indicator is used, photoelectric methods are applicable. In these respects, it resembles a wide variety of reaction of recent interest, especially in the field of biochemistry, on the study of which all the resources of modern instrumental analysis have been lavished. Since the dehydration of H_2CO_3 is an easily performed reaction in a convenient velocity range, it has been examined with several different kinds of apparatus; but in most of this work it is clearly the instrument performance, not the reaction, which is uppermost in the author's mind.

Dalziel (*29*) for example replaced the automobile headlamp and Cu_2O photocell of Brinkman's original rapid flow apparatus with a Beckman spectrophotometer. The mixer and observation tube assembly were moved on a track to bring various points to the observation site.

Schwarzenbach (*30*) on the other hand substituted electrometric *p*H measurement with a series of four glass electrodes. The electrode spacing was such that observations were mostly towards the end of the dehydration reaction when the reverse reaction had become important. Nevertheless, he observed what appeared to be an anomalously high rate in the first 0.05 sec of the reaction, which led him to suggest a $(H_2CO_3)^2$ term in the rate law, corresponding to the parallel mechanism

$$2H_2CO_3 \rightarrow HCO_3^- + H_2CO_3^+$$

$$H_2CO_3^+ \rightarrow CO_2 + H_3O^+$$

This result has not as yet been confirmed by other investigators.

Several workers have applied the stopped flow technique. This was originally used by Roughton to extend the measurable half life of reactions in his rapid flow observation tube. If the flow was suddenly halted, the progress of a slow reaction could be conveniently followed by continuous observation at a fixed point in the tube. By introducing electronic recording, Chance (*26*) made it possible to follow reactions with half lives of a few hundredths of a second. The main function of the rapid flow assembly was to provide almost instantaneous mixing prior to a static rate measurement, usually recorded on an oscillograph. The initial spurt of mixed solution was provided by a sudden push on a pair of syringes. The great advantage of this method over the continuous flow is the very small volume of solutions required, just enough to rinse and fill a short capillary tube. Though this feature is important in biological studies, it hardly weighs in the balance for the study of CO_2 kinetics. Nevertheless, the method has been used with excellent results, primarily for testing purposes.

Gibson (*31*) and Scheurer (*32*) have determined $k_{H_2CO_3}$ over a range of temperatures using stopped flow spectrophotometric measurements combined with oscillographic recording. Sirs (*33*) used a glass electrode. The response of such electrodes is extremely rapid. His results agree well with those of the others, but they all lie significantly below the thermometric values of Roughton. This discrepancy has not yet been explained. The results are compared in Table 2.

Table 2. Values of $k_{H_2CO_3}$ corrected to 18° (assuming E_A = 16.5 except where otherwise noted)[a]

Author	Method[b]	Exp'tal k (T)	$k_{18°}$	E_A kcal
Faurholt (1924)	Quenching	2.3 (0°)	15.0	..
Saal (1928)	H_2 electrode	12.5 (20°)	10.3	..
	Conductometric	8.0 (13.5°)	12.5	..
Brinkman (1933)	Photoelectric	10.2 (15°)	12.9	..
Roughton (1941)	Thermometric	(0–38°)	14.6	16.5
Dalziel (1953)	Photoelectric	(19°–23°)	12.3	16.9
Gibson (1955)	Stopped flow photoelectric	12.5 (19°)	11.4	..
Schwarzenbach (1957)	glass electrode	10.0 (20°)	8.2	..
Scheurer (1958)	St. fl. photoelec.	(23°–35°)	11.8	16.1
Sirs (1958)	St. fl. glass elec.	(0°–35°)	12.3	16.9

[a] All data were obtained in HCl-NaHCO mixtures.
[b] All except the first method involved rapid or stopped flow.

Hydration: $CO_2 + H_2O \xrightarrow{k} H_2CO_3$

This reaction cannot well be studied (isotopic exchange aside) except in slightly basic buffers (*p*H 7–8) which favor the forward direction while still snppressing the OH^- mechanism. Under these conditions the half life at low temperatures is several minutes. The manometric method is preferred because of its simple operation and its direct measure of the CO_2 concentration. In the hands of Roughton and co-workers (*34*) it has become a high precision technique. Buffer catalysis is allowed for by measurements in buffers of diminishing strength and extrapolation to zero concentration. Studies by Roughton have further shown the need for a diffusion correction arising from the presence of diffusion gradients in the gaseous phase during the early, faster period of the reaction. To correct for the reverse reaction, the reversible form of the first order equation is used as described above under Faurholt's work, K_a being determined from the CO_2 present at equilibrium. Above all, recent work on k_{OH} has shown that the competing mechanism, while

negligible at 0°, assumes a greater relative importance at higher temperatures, amounting to 40% of the total at 38°, even at *p*H 7.5. A radical correction is therefore necessary.

The plot of ln k_{CO_2} versus $1/T$ shows considerable curvature (Fig. 1); the apparent activation energy drops from 19 to 11 kcal as the temperature rises from 0°–40°. This behavior has been noted in other reactions between solvent and solute, such as hydrolysis. Analysis according to the method of Moelwyn-Hughes (*35*) yields a true activation energy of 79 kcal.

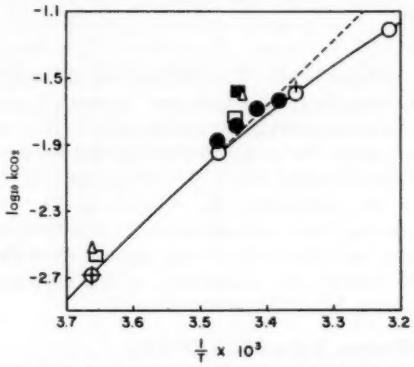

Figure 1. Plot of log k_{CO_2} against $1/T$. The solid line follows Pinsent's data. For the dotted line, see text. ○ Manometric (Pinsent 1951, 1956). ● Photometric (Perrin; See Pinsent 1951). + Isotopic exchange (Urey 1940). □ Manometric (Brinkman 1933). ■ Photometric (Brinkman 1933. △ Quenching (Faurholt 1924). The last three show the effects of uncorrected buffer catalysis.

With characteristic experimental virtuosity, the Cambridge group have confirmed k_{CO_2} by several other methods, although the manometric results are considered definitive. The application to this reaction of the photoelectric *p*H method, pioneered by Brinkman, *et al.*, and much used in studies of carbonic anhydrase activity, was brought up to date by Clark and Perrin (*36*) who adapted it to the stopped flow technique. They automatically recorded the changing optical density of phenol red in stopped mixtures of CO_2 and buffer, using the method of Chance. The same authors revived Faurholt's original carbamino quenching technique. The limitation imposed by his crude mixing method was surmounted by combining CO_2 and buffer solutions in the rapid flow apparatus; after a fixed time of passage through the observation tube, the mixture was ejected into a concentrated solution of dimethylamine. To sharpen the quenching operation, Pinsent (*37*) forced dimethylamine into the flowing stream by way of a second mixer built into the end of the tube.

The Basic Mechanism: $OH^- + CO_2 \xrightarrow{k} HCO_3^-$

Recent measurements of k_{OH} have been carried out primarily as an adjunct to the k_{CO_2} work, but also with important practical applications in mind which include the interaction of CO_2 with the more alkaline biological secretions and the absorption of CO_2 in various industrial processes. In fact, Pinsent and coworkers (*38*) measured k_{OH} in a wide range of neutral salt concentrations specifically to serve the needs of chemical engineers.

Previous work was done either in buffers *p*H 10–11 (primarily carbamino and manometric) or NaOH solutions (rapid flow conductometric and photoelectric *p*H). When buffers are used, (OH^-) at any stage in the reaction depends on the buffer ratio, the buffer K_a, and various activity coefficients. The buffer ratio in turn is related stoichiometrically to the CO_2 concentration through the equation

$$CO_2 + B^- + H_2O \rightarrow HB + HCO_3^-$$

Thus (OH^-) and (CO_2) can be expressed in terms of each other, and either can be used as the experimentally determined variable in the second order rate law (equation (6)). The integrated form is a complex expression which requires an elaborate ionic strength correction. This was applied only in a rough way to the early work which suffered thereby an inherent loss of accuracy.

The situation in NaOH solutions is mathematically much more straightforward. The normal second order treatment, when applied to the net reaction

$$2OH^- + CO_2 \rightarrow CO_3^{--} + H_2O$$

yields the equation

$$kt = \frac{2.3}{b - 2a} \log \frac{b - 2y}{a - y} + \text{constant}$$

where a and b are the initial CO_2 and OH^- concentrations, and y is the concentration of reacted CO_2 at any instant; y is directly determinable from rapid CO_2[7], OH^- (*p*H), or thermal measurements. The influence of ionic strength is minor. The latter moreover usually does not exceed 0.01, in contrast to the unavoidably high strengths of buffer solutions.

In the course of their manometric work on k_{CO_2}, Pinsent and Roughton (*34*) carried out similar measurements on k_{OH} in carbonate-bicarbonate buffers (*p*H 10) with all the appropriate precautions, corrections, and extrapolations. The method could not be used above 10° because the very fast absorption at high temperatures posed special experimental problems. These were avoided in later work (*38*) by the use of a less basic buffer; but this means of slowing the reaction had the undesired effect of favoring the direct hydration mechanism. A correction could of course be made, once k_{CO_2} was accurately known. Since the k_{OH} measurements were designed in part to help obtain an accurate k_{CO_2}, it is clear that the manometric method could not be used as a primary one.

Pinsent and co-workers (*38*) accordingly turned to the thermometric method, which is ideally suited to the reaction in NaOH solutions. Using a high speed (3 m/sec) well thermostated apparatus, they managed in a typical run to obtain nine temperature readings over the first ten milliseconds. The plot of ln k versus $1/T$ yields an excellent slope corresponding to an activation energy of 13.2 kcal (Fig. 2).

This work has recently been rounded off by Sirs,

[7] An "aerotonometric" method of analyzing dissolved CO_2 in rapid flow systems, developed by M. Dirken and H. Moonk, *J. Physiol.*, **70**, 382 (1930), has been much described and little used. It measures the rate at which CO_2 gas is absorbed by a jet of reaction mixture during passage through a small CO_2-filled space.

stopped flow experiments with NaOH-CO_2 mixtures (*39*). In one setup he measured OH^- spectrophotometrically, with the aid of a suitably basic indicator (Tropaeolin 0). In another, he measured conductance in a revival of Saal's approach. Both techniques gave him low results, which were however in agreement with Brinkman's early work by the optical method. In a clever piece of detective work he succeeded in tracing the discrepancy to the formation of CO_2 bubbles during turbulent flow. This created a systematic error by lowering the light absorption and conductivity of the solution, thus diminishing the apparent OH^- concentration.[8] The use of only one quarter saturated CO_2 as his reagent solution overcame the difficulty. The consistent results secured by these and three other entirely independent methods (Fig. 2) over a ten thousandfold range of OH^- must represent some kind of record in the history of reaction kinetics.

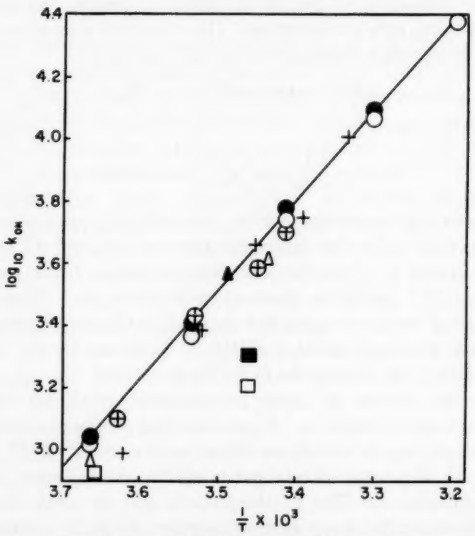

Figure 2. Plot of log k_{OH} against $1/T$. The straight line corresponds to an activation energy of 13.2 kcal. ○ Manometric (Pinsent 1951, 1956) ● Thermometric (Pinsent 1956) + Photometric (Sirs 1958) ⊕ Conductimetric (Sirs 1958) ▲ Conductimetric (Saal 1928) □ Manometric (Brinkman 1933) ■ Photometric (Brinkman 1933) △ Quenching (Faurholt 1924) Note the astonishing accuracy of Faurholt's method in this very rapid reaction.

The True Dissociation Constant of H_2CO_3

The determination of this quantity, which was a major goal of the early work, was later subordinated to the investigators' kinetic interests. Several authors (*30*, *32*) have recently revived Saal's zero-time *p*H method, for which the latest rapid mixing apparatus is well-adapted. The new values are significantly lower than the earlier ones (Table 3).

Their results stand confirmed by the entirely independent high field conductance method (*40*). When solutions of weak electrolytes are subjected to alternating fields of up to 200 kv/cm, there is superimposed on the usual Wien effect a further enhancement of the conductivity caused by the increased dissociation in the high voltage field. The calculation of dissociation constants from such data does not require a knowledge of the weak electrolyte concentration. The method therefore avoids the root difficulty of the H_2CO_3 problem. Measurements in CO_2 solutions of 5°–45° showed a low maximum, $K_a = 1.76 \times 10^{-4}$ at 17°. The ionization heats calculated from this temperature dependence unfortunately do not agree well with those measured directly by Roughton, which corresponded to a maximum K_a at 55° rather than 17°.

[8] From Figure 2 it appears that Saal's experiments were free from this disturbing effect.

Table 3. K_a Values Obtained by Various Workers[a]

Worker	$K \times 10^4$	Temperature
Thiel (1914)	1.9	4°
Faurholt (1924)	2	0°
Saal (1928)	3.1	13°
Brinkman (1933) (by combining $k_{H_2CO_3}/K_a$ with his best direct photoelectric $k_{H_2CO_3}$	2.4	15°
Roughton (1941)	2.5–3.4	0°–38°
Wissbrun (1954)	1.56–1.76–1.60	5°–17°–45°
Schwarzenbach (1957)	1.7	20°
Scheurer (1958)	1.8–1.3	25°–35°

[a] The early work is difficult to evaluate because of inadequate correction for ionic strength. The dissociation is almost double at $\mu = 0.1$ (Harnee, H., and Bonner, F., *J. Am. Chem. Soc.*, **67**, 1026 (1945).

The Equilibrium Ratio $(CO_2)/(H_2CO_3)$

This constant can be calculated from two independent sets of data since $K = k_{H_2CO_3}/k_{CO_2} = (K_a/K_1) - 1$. It would be pleasant to end this review on a note of finality, but it is apparent from the comparison below that the last word on the subject is yet to be said. Values of $k_{H_2CO_3}$ are based on the figure 12.3 for 18° and an activation energy of 16.5 kcal; k_{CO_2} has been read off the solid curve in Figure 1; K_1 is from the work of Harned and Davis (*41*) and K_a from Wissbrun, *et al.* (*40*).

t°	0	5	15	25	35	38
$K = (K_a/K_1) - 1$	...	515	463	386	340	...
$K = k_{H_2CO_3}/k_{CO_2}$	950	890	810	930	1120	1230
K from Roughton (*21*)	950	...	780	720	...	680
$K = k_{H_2CO_3}/k'_{CO_2}$	950	...	810	760	...	680

Roughton has also published K's for various temperatures (row 3 above). His 0° value is obtained from the rate constant ratio, since at that temperature the kinetic data are most reliable. The others are based on this value plus his ΔH measurements for the dehydration reaction (*25*). It is interesting to note that the temperature dependence predicted from his thermometric data corresponds very well with that obtained from the rate constant ratio, if log k_{CO_2} is allotted a conventional linear temperature dependence (dotted line Figure 1, and row 4 above).

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What is Clinical Chemistry?—A Vocational Conversation

All too often in the selection of his life work, the student has only a vague knowledge of the relationship of his chosen vocation to the world at large. The chemist can provide a service (chemical analysis), develop and exploit new ideas (chemical research and development), transmit chemical ideas to others (chemical education), and direct the operations of a research or processing laboratory (chemical management). An adjunct to all of these areas of work is that of chemical literature and the chemical librarian. For chemistry students a knowledge of its ramifications is as important as the specific details about any particular job. The clinical chemist who is well trained and takes his varied career seriously is at one and the same time an analyst, an investigator, an educator, and an administrator.

Clinical chemistry is a synthesis of the multiple disciplines of chemistry in their application to analytical problems in clinical medicine. By extending analytic procedures to biological tissues and modifying methods so that they are applicable to smaller and smaller biological samples (ultramicro analysis), the clinical chemist has made it possible for the physician to obtain objective data as an aid to diagnosis and prognosis. In addition to studies in methodology, the ultimate aim of clinical chemistry is to study the biochemical aspects of disease. The object of such investigations is to attempt to elucidate the biochemical lesions of disease and to understand the disease process and its metabolic consequences with the hope of placing diagnosis and therapy on a rational basis.

The functions of the clinical chemist-educator are as varied as those of any other educator. He will teach methodology to student technicians, biochemistry and clinical biochemistry to medical students, interns, residents, and established physicians. His educational services to the graduate physician will provide a means for the physician to keep abreast of advances in medical science.

In the large voluntary, community, or teaching hospital, the clinical chemist must also be an efficient administrator. He directs the work of a number of technicians in the analytical and research laboratories, appoints new employees, purchases equipment and chemicals, and directs a well-rounded teaching program. Preparation for a career in clinical chemistry requires the usual undergraduate training in chemistry with graduate training leading to a master's degree and preferably to a doctorate in biological chemistry.

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NSF Fellowship Programs

Support of graduate training in chemistry

Fellowships are an instrument of service to selected individuals in the form of grants to enable those individuals to further their scholarly pursuit of knowledge. They are investments in the future of individuals of high potential and are hence long-range investments in the future of our nation. They are clearly distinct from grants designed to underwrite a specific project—research or development—and do not normally require any services to be rendered by the recipient.

The NSF supports seven fellowship programs at the graduate or postdoctoral levels, each designed to meet a specific need. Section 10 of the National Science Foundation Act authorizes the Foundation to offer fellowships and prescribes certain provisions that govern their administration. Among the latter are the following: (1) the fellows shall be selected by the Foundation from among citizens of the United States solely on the basis of ability; (2) the fellows shall have freedom of choice of their institutions from among appropriate nonprofit American or nonprofit foreign institutions; (3) when there are several applicants judged to be of substantially equal ability and there are insufficient funds to offer a fellowship to each, the awards will be offered in such a way as to achieve an equitable geographic distribution; and (4) the awards may be offered for scientific study or scientific work in the mathematical, physical, medical, biological, engineering, and other sciences.

In the administration of its fellowship programs the Foundation, in addition, follows certain principles as a matter of policy. The essential features of policy are the following: (1) the selection of fellows shall be made following, without exception, the advice of evaluation panels of highly competent scientists selected for this task by reputable national organizations; (2) because fellowships are long-range investments in the competence of individuals and not suitable mechanism for meeting immediate shortages of specific kinds of scientific manpower, and because there is no way of accurately predicting the numbers of each kind of scientific specialists that will be needed, say, ten or twenty years hence, NSF fellowships are not awarded preferentially in any specific fields of science; and (3) all applicants in each program shall compete as individuals in a national competition.

Awarding fellowships is one of several approaches being used by the NSF in seeking solutions to the difficult and complex problems confronting the United States in science education and scientific and technological leadership. The seven fellowship programs currently supported by the NSF offer a wide range of opportunities for training to graduate students, advanced scholars, and college and secondary school teachers—all of whom contribute to the nation's scientific effort. Announcements and other literature on each program are available upon request from the Foundation. These programs are summarized here as follows[2]:

Fellowships for Graduate Students—(1) Graduate; (2) Cooperative Graduate; and (3) Summer Fellowships for Graduate Teaching Assistants.

The first two programs are designed to offer support to unusually able students, but differ in operational details and institutional participation. The third program is designed to enable selected graduate teaching assistants to devote full time in the summer to their own studies.

Fellowships for Research Scientists—(4) Postdoctoral; and (5) Senior Postdoctoral.

These programs offer support to individuals who have received doctoral degrees and who immediately or some years later desire or need additional training to further improve their competence as research investigators.

Fellowships for Teachers—(6) Science Faculty; and (7) Summer Fellowships for Secondary School Teachers of Science and Mathematics.

These programs offer support to teachers seeking further scientific training to increase their competence as teachers.

Extramural Programs—In addition to the seven National Science Foundation fellowship programs listed above, the Foundation is now engaged in a new, extramural type of fellowship activity, namely, the administration of the North Atlantic Treaty Organization (NATO) Postdoctoral Fellowships in Science. This program has been funded by the Department of State. It appears likely that the Foundation will administer additional fellowship programs for other agencies funded from sources other than National Science Foundation appropriations. Twenty NATO fellowship awards were made in May, 1959, and it is assumed, at this time, that additional awards will be offered next year.

Of the seven NSF fellowship programs, three are new this year and were designed to fill specific needs—(*a*) Cooperative Graduate Fellowships; and (*b*) Summer Fellowships for Graduate Teaching Assistants; and (*c*) Summer Fellowships for Secondary

[1] Head, Fellowships Section, Division of Scientific Personnel and Education. A similar report on engineering was presented at the 67th Annual Meeting of the American Society for Engineering Education, June 15–19, 1959, Pittsburgh, Pennsylvania, and submitted for publication in the *Journal of Engineering Education*. Reports on NSF support of graduate training in physics, mathematics, and the life sciences will be submitted for publication to appropriate journals in the respective fields.

[2] Specific details (e.g., application deadline dates) and full information appear in the pamphlet "National Science Foundation Programs for Education in the Sciences" available from the NSF, Washington 25, D. C.

Table 1. Summary of NSF Fellowships

Fiscal year	Applicants	No. fellows	Applicants	No. fellows	Applicants	No. fellows	Applicants	No. fellows	Totals: Applicants	Totals: No. fellow
	Graduate		Postdoctoral		Senior postdoctoral		Science faculty			
1952	2685	537	283	38	..	..	..	..	2968	575
1953	2930	498	368	24	..	..	..	..	3298	522
1954	2865	631	461	59	..	..	..	..	3326	690
1955	2931	657	458	53	..	..	..	..	3389	710
1956	2892	715	508	79	159	35	..	..	3559	829
1957	3028	773	482	85	304	48	416	100	4230	1006
1958	3804	939	513	125	259	70	694	214	5270	1348
1959	4506	1100[a]	778	194[a]	241	83[a]	1069	302[a]	...	...
	Cooperative graduate		Graduate teaching assistants		Secondary school teachers					
1959	2872	1050[a]	1260	580[a]	1578	628[a]			12,304	3937[a]

[a] Awards offered in fiscal year 1959, as distinguished from acceptances in previous years.

It is anticipated that declinations, after awards have been offered will amount to approximately 6% (varying from less than 2% in the Science Faculty program to as high as 15% in the Postdoctoral program) for all programs considered collectively, or that of the 3937 awards offered, 3700 will be accepted.

School Teachers. A summary of NSF fellowship programs is given in Table 1.

It is significant to note that there was a marked increase in applicants (4506) in the Graduate program this year as compared to 1958 (3804) and this despite the fact that 2872 other applicants of substantially equal ability distribution applied in the new Cooperative Graduate program. Many people have wondered if there were any advantages in applying in one over another of these programs. The Foundation operated these programs in such a way as to insure comparability in the evaluation of all applicants. There is one point which may not be self-evident from the table; namely, of the 1100 awards in the Graduate program, 549 were to renewal applicants and 551 to new applicants. Since there were 3857 new applicants, the ratio of awards to applicants in this "new" group was 1:7, representing one of the keenest competitions for new awards in the history of the NSF predoctoral fellowship program.

The financial support for NSF fellowship programs is shown in Figure 1. It is evident that the major growth in financial support corresponds to the expansion into new fellowship program areas in fiscal year 1959. We estimate that the seven NSF programs in 1960 will operate at approximately the same levels as in 1959.

It is significant to note, as given in Table 2, the extent to which applicants in the field of chemistry participated in the fiscal year 1959 program. Since the National Science Foundation classifies biochemistry under Life Sciences, the data on biochemistry applicants and awards offered in each fellowship program, listed in Table 2, are as follows: Graduate, 137 applicants and

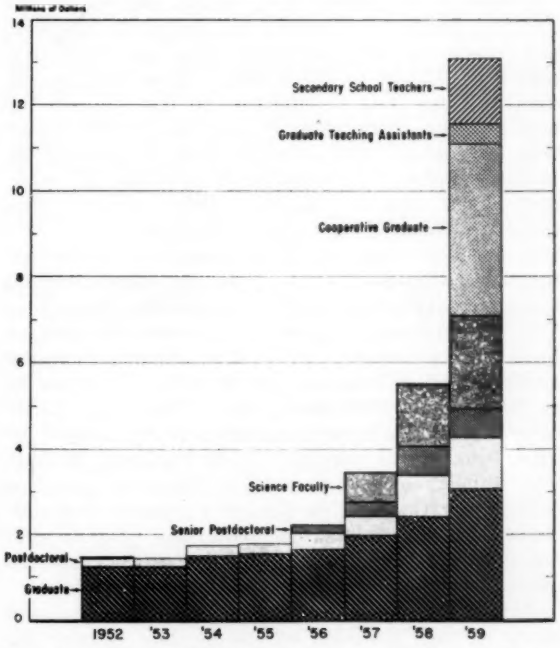

Figure 1. Distribution of NSF fellowship funds by programs, fiscal years 1952–59.

Table 2. Distribution of Applicants and Awards Offered by Field of Study for Fiscal Year 1959

Field	Graduate: Applicants	Graduate: Awards offered	Cooperative graduate: Applicants	Cooperative graduate: Awards offered	Teaching assistants: Applicants	Teaching assistants: Awards offered	Postdoctoral: Applicants	Postdoctoral: Awards offered	Senior postdoctoral: Applicants	Senior postdoctoral: Awards offered	Science faculty: Applicants	Science faculty: Awards offered
Physical Sciences												
Astronomy	43	13	12	5	2	0	1	0	1	0	5	2
Chemistry	787	201	580	205	368	162	156	36	43	12	118	32
Earth Sciences	283	75	161	50	80	39	27	7	15	4	41	9
Engineering Sciences	807	175	534	233	128	59	12	3	19	5	294	83
Mathematical Sciences	531	143	263	128	129	71	54	30	16	6	209	58
Physics	906	259	454	178	124	62	102	42	34	13	111	33
General	...	...	...	...	...	...	...	...	...	...	12	1
Subtotal	3357	866	2004	799	831	393	352	118	128	40	790	218
Life Sciences	1041	216	785	238	369	165	404	73	107	40	268	83
Selected Social Sciences	108	18	83	13	60	22	22	3	6	3	...	...
Natural Sciences, general	...	...	...	...	...	...	...	...	...	...	11	1
Total	4506	1100	2872	1050	1260	580	778	194	241	83	1069	302

Table 3. NSF Graduate and Cooperative Graduate Fellowship Programs for Fiscal Year 1959, Distribution of Awards Offered by Field and Level (Physical Sciences)

Field	Graduate				Cooperative graduate				Grand total
	First year	Intermediate	Terminal	Total	First year	Intermediate	Terminal	Total	
Physical Sciences									
Astronomy	5	4	4	13	1	3	1	5	18
Chemistry	61	81	59	201	32	109	64	205	406
Earth Sciences	17	37	21	75	9	24	17	50	125
Engineering	80	74	21	175	117	82	34	233	408
Mathematics	56	61	26	143	28	54	46	128	271
Physics	95	103	61	259	30	101	47	178	437
Subtotal	314	360	192	866	217	373	209	799	1665
Life Sciences	71	91	54	216	43	140	55	238	454
Selected Social Sciences	5	8	5	18	2	6	5	13	31
Total	390	459	251	1100	262	519	269	1050	2150

30 awards; Cooperative Graduate, 107 and 38; Teaching Assistants, 24 and 13; Postdoctoral, 68 and 16; Senior Postdoctoral, 23 and 11; and Science Faculty 17 and 6, respectively. In the Graduate and Cooperative Graduate programs, 406 of the 1367 applicants in chemistry were offered awards, which are divided almost equally between the two programs.

Chemistry applicants and awards offered in the Teaching Assistants, Postdoctoral, Senior Postdoctoral, and Science Faculty fellowship programs were at a high level relative to other fields. In addition to the data in Table 2, it is important to note that in the new program of Summer Fellowships for Secondary School Teachers, 258 chemistry and 11 biochemistry teachers applied (1578 total applicants) and 82 and 9, respectively, received awards. Other general relationships will be evident upon study of Table 2.

Some of the more significant aspects of the participation of chemistry students in the Graduate and Cooperative Graduate programs are given in Table 3.

In this table applicants receiving awards are grouped by field and year level. Of the 406 combined chemistry applicants offered awards, only 93 (or 22.9%) would be at the first-year level during the academic year 1959–60—thus, each of these programs provides support for intermediate and terminal level students, mainly. The number of first-year level chemistry awardees (32) in the Cooperative Graduate program is significantly less than in the older Graduate program (61) for approximately the same number of total awards offered in all fields in each program.

Applicants in the Cooperative Graduate program apply through graduate schools of their choice; the institutions evaluate all applicants and then forward all applications to the NSF along with a rank ordered list of their recommended applicants and a list of all non-recommended applicants. All applications are further evaluated by a central panel, which takes into account the institutions' evaluations, and the Foundation then selects the awardees, based on the recommendations of the central panel and in accordance with statutory requirements. A special feature of the Cooperative Graduate program is that each institution receives $1800 to aid in covering costs of education of the fellow, including tuition and required fees. This program is designed in such a way as to insure a wider distribution of support and strengthening of graduate institutions on a broadened institutional base.

The distribution of chemistry Graduate and Cooperative Graduate fellowship applicants and awards offered in fiscal year 1959, by fields of specialization, is given in Table 4. For biochemistry, the number of applicants is 132 and 107, respectively, and awards offered is 30 and 38, respectively, in each program.

The fields of specialization listed are those designated by the applicants and, therefore, are not a classification of applicants by the Foundation. The information in this table—and in other tables to follow—is arranged in such a way as to make possible the ready comparison between the two predoctoral programs, their applicants, and awards, using the older program (Graduate) as the base. Many interesting comparisons between fields of specialization are evident.

Each year, as an integral part of the Foundation's work and in an attempt to make pertinent information available to all interested parties, we bring together additional data on the geographic distribution of applicants and awardees, the baccalaureate origin of awardees, and a list of institutions the awardees plan to attend. Although some awardees change to other schools for a number of reasons, for purposes of presenting information on our fiscal year 1959 operations, it has not been possible to take this into account.

The distribution of chemistry (exclusive of biochemistry) Graduate and Cooperative Graduate fellowship applicants and awards by state of permanent residence if given in Table 5.

In the Graduate program, applications were received from people in 48 States, territories, and the District of Columbia, but only 47 were represented in the Cooperative Graduate program. This latter situation probably arose from the fact that the Cooperative Graduate program was new this year. For purposes

Table 4. NSF Graduate and Cooperative Graduate Fellowship Programs for Fiscal Year 1959, Distribution of Chemistry Fellowship Applicants and Awards Offered by Field of Specialization

Field	Graduate program		Cooperative graduate program	
	Applicants	Awards offered	Applicants	Awards offered
Physical	296	89	230	98
Organic	276	74	227	72
Chemistry (not elsewhere classified)	64	11	19	4
Inorganic	62	8	39	13
Theoretical	45	15	17	6
Analytical	38	4	29	7
Pharmacological and Pharmaceutical	3	0	17	5
Agricultural	2	0	1	0
Geochemistry	1	0	1	0
Total	787	201	580	205

of presentation, we have arbitrarily arranged the first part of Table 5 in order of descending number of applicants in the Graduate program, and have used as a cut-off point 12 applicants. This method of presentation is solely for the purpose of focusing attention on differences between the two programs and is intended in no way to reflect on applicants from any state. Indeed, these data will vary from year to year, but they are presented in the hope that others interested in the educational problems of the nation will find them of value. In the Graduate program, the persons from the first twenty states listed in Table 5 account for 86.4% of the chemistry applicants and 80.6% of the awardees; in the Cooperative Graduate program the figures are 80% and 75.6%, respectively.

Table 5. NSF Graduate and Cooperative Graduate Fellowship Programs for Fiscal Year 1959, Distribution of Chemistry Fellowship Applicants and Awards Offered by State of Permanent Residence

State	Graduate program		Cooperative graduate program	
	Applicants	Awards offered	Applicants	Awards offered
New York	124	34	82	30
Illinois	68	9	44	14
California	67	17	33	14
Pennsylvania	56	9	45	19
Massachusetts	47	9	20	3
Ohio	36	9	44	8
Minnesota	28	6	13	4
Michigan	27	13	22	6
New Jersey	25	9	29	9
Wisconsin	21	12	5	1
Maryland	19	3	10	3
Texas	18	6	29	12
Kansas	15	5	13	6
Indiana	14	1	23	6
Missouri	14	3	13	4
Tennessee	13	5	9	3
Florida	12	2	9	6
Kentucky	12	2	8	4
North Carolina	12	4	6	1
Washington	12	4	5	2
Subtotal	640	162	462	155
29 other states	147	39	118	50
Total	787	201	580	205

In Table 5, the data are for chemistry (exclusive of biochemistry) applicants and awardees at all graduate year-levels. Data on baccalaureate origin of first-year-level awardees are given in Table 6 for the Graduate program and Table 7 for the Cooperative Graduate program. Although 45 institutions are represented in the Graduate program and 27 in the Cooperative Graduate program, only five are represented in both programs, and for this reason separate tables have been prepared. Thus, a total of 72 institutions is represented in the two programs. The tables are set up in descending order of awardees from each institution. The fact that applicants from 22 different institutions were successful in the Cooperative Graduate program as compared to the older Graduate program would emphasize that capable students are present in other schools and perhaps what the Foundation has done is to broaden the base for participation by giving the cooperating institutions an opportunity to analyze their own needs more clearly. The Foundation is not evaluating institutions, however, but rather reporting the results of a single year's competition.

Now, where do chemistry applicants who are offered awards say they wish to attend school? For the fiscal year 1959 Graduate and Cooperative Graduate programs, this question is answered in Table 8. As mentioned earlier, this listing is subject to change by declinations and changes in institutions for a number of reasons once the awards are offered. For purposes of presentation, Table 8 has been arbitrarily divided into two parts, the first part consisting of a listing in descending order of combined year level awardees for the first 20 institutions in the Graduate program, and the second part arbitrarily grouping together the institutions chosen by two or more awardees in The Graduate Program.[3] In the Graduate program there are 40 institutions indicated by awardees whereas in the Cooperative Graduate program 67 institutions are represented. It should be mentioned that the University of Cambridge (England) was not eligible to compete in the Cooperative Graduate program. Chemistry awardees designating the first six institutions listed in Table 8 as their proposed institution account for 63.7% of the combined-year level awardees and 73.8% of first year level awardees in the Graduate program. By contrast, awardees choosing the same institutions in the Cooperative Graduate program amount to only 22.4 and 18.8%, respectively. It must be remembered that,

Table 6. NSF Graduate Fellowship Program for Fiscal Year 1959, B.A. Institutions of First Year Chemistry Awardees

Institution	Awardees
Mass. Inst. of Tech.	5
Harvard, Yale	4
Carnegie Inst. of Tech.	3
Kalamazoo Coll., Michigan, Wisconsin, St. Olaf	2
Other colleges and universities (each) Albion, Amherst, Antioch, Barnard, Brown, Cal. Tech., William & Mary, Dartmouth, Fordham, Furman, Loyola (La.), Marquette, Michigan Mining & Tech., Middlebury, Oberlin, Occidental, Ohio U., Brooklyn Polytech., Princeton, Rensselaer, Rice, Rutgers, Douglass, Spring Hill, Swarthmore, California (Berkeley), Chicago, Delaware, Minnesota, North Carolina, Notre Dame, Pennsylvania, Tennessee, Texas, Washington, Vanderbilt, Western Reserve	1
Total	61

Table 7. NSF Cooperative Graduate Fellowship Program for Fiscal Year 1959, B.A. Institutions of First Year Chemistry Awardees

Institution	Awardees
Colorado	3
Georgia Tech., Queens, Illinois	2
Other colleges and universities (each) Antioch, Boston, Calvin, Wooster, Duke, Grinnell, Lebanon Valley, Oberlin, Oklahoma A. & A. S., Oregon State, Purdue, St. John's (N. Y.), St. John's (Minn.), Arkansas, California (Berkeley), Georgia, Minnesota, Pittsburgh, Rochester, Tennessee, Wagner, Whitman, Wilson	1
Total	32

[3] EDITOR'S NOTE: The details of this table were deleted as a space-saving procedure. Readers desiring the complete list of institutions can obtain it by writing either the author or the editor.

Table 8. NSF Graduate and Cooperative Graduate Fellowship Programs for Fiscal Year 1959, Institutions Chosen by Chemistry Applicants Offered Awards

Institution	Graduate program		Cooperative graduate program	
	First year	Combined levels	First year	Combined levels
Harvard	14	36	0	6
California Inst. of Tech.	9	24	0	1
California (Berkeley)	15	23	1	13
Mass. Inst. of Tech.	1	17	0	5
Wisconsin	4	17	2	7
Illinois	2	11	3	14
Columbia	0	7	0	9
Princeton	1	7	0	5
Northwestern	2	5	0	3
California (Los Angeles)	1	4	0	4
Chicago	1	4	0	4
Duke	0	3	1	1
Ohio State	0	3	1	6
Kansas	0	3	0	3
North Carolina	1	3	0	1
Washington	0	3	0	4
Yale	1	3	0	2
Cornell	1	2	1	6
Florida State	1	2	0	1
Brooklyn Polytech.	0	2	0	0
Subtotal	54	179	9	95
Twenty Institutions, including Cambridge, (England)	7	22	—	—
Forty seven Institutions	—	—	23	110
Total	61	201	32	205

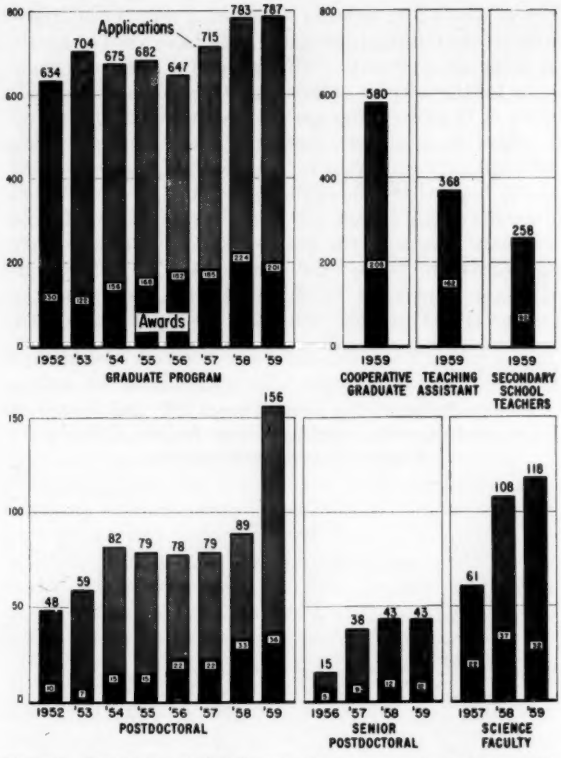

Figure 2. Distribution of NSF chemistry fellowship applicants and awards offered, fiscal years 1952–59.

although it had been hoped that the Cooperative Graduate program would produce a wider distribution in all fields, we could not have predicted in advance that the distribution of chemistry awardees would have been as given in Table 8. Neither could it have been predicted that an almost equal number of awards would go to chemistry applicants in both programs. Many of the results obtained in this year's competition for chemistry may not be reflected in other fields, and studies are currently under way to make available similar data in other fields.

In summary, it can be stated that chemistry applicants have competed favorably with applicants in other fields for NSF Fellowships and the new Cooperative Graduate program has not increased appreciably the number of first-year level awards. Just how chemistry (exclusive of biochemistry) applicants have fared from 1952 through 1959 is shown in Figure 2.

The National Science Foundation fellowships are designed to encourage excellence in individuals, irrespective of scientific fields or financial need and it is hoped that they will serve as a friendly competitive force in our educational system. Selection of the very best individuals from among the many thousands of capable people who apply, on their own initiative, continues to challenge the Foundation. There are insufficient predictors to guarantee an absolute degree of selection of "sure winners" only, but on the basis of available information and information obtained through research on selection techniques supported by the Foundation, we strive to identify those highly capable individuals and provide them with reasonable finanical support for their scientific development. Because the stakes are high and the nation can ill afford to put too little emphasis on science training and its chemists, engineers, mathematicians, and other scientists in this competitive era, we hope that our combined fellowship programs will have a significant and favorable impact on science in the United States.

The number of college juniors who elected science and mathematics as their major increased 10.4% between the fall of 1957 and the fall of 1958. In its second annual survey of "Junior-Year Science and Mathematics Students" (U.S. Department of Health, Education, and Welfare Cir. No. 577), the Office of Education found that 55,777 students were registered for majors in science and mathematics, as compared with 50,513 one year earlier. Third-year engineering students numbered 47,198, off 2.5% from the preceding year. In combination, junior enrollments in engineering and science, including mathematics, comprised 25% of the junior student body.

Engineering and Scientific Manpower Newsletter, November 2, 1959

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Is Chemical Information Growing Exponentially?

In an earlier article[1] the authors stated that the amount of chemical information was doubling every thirteen years. It is the purpose of this note to summarize data bearing on this point.

Chemical Abstracts

Table 1 gives the number of lines in the decennial subject indexes of *Chemical Abstracts* since 1907. It was felt that the subject indexes represented the best measure of chemical information available.

In order to find a relation between total chemical information and time, it was necessary to estimate an initial value for the lines of *Chemical Abstracts* equivalent to all chemical information prior to 1907. Mere extrapolation backwards of the curves did not seem justified, since the geometric increase in information might be a phenomenon of the twentieth century. An estimate of the relation of total information prior to 1909 and information published from 1910–1919 was obtained from Beilstein's "Handbuch der Organischen Chemie." The main work covering literature up to 1909 is approximately twice as large as the supplement for 1910–1919. Assuming that Beilstein really does abstract all of organic chemistry prior to 1909 and that a similar relation holds for the whole of chemistry, and given that the number of lines in the decennial subject index to *Chemical Abstracts* for 1907–16 is 3.6×10^5, we took the cumulative total for 1906 to be equivalent to 8×10^5. If the order of magnitude is reliable, then the exact value is not particularly important in the cumulative totals.

Table 2 gives the cumulative totals including this base figure. The data are plotted in Figure 1. The open circles are for the logarithm of the total lines while the filled circles are for the arithmetic totals.

Table 1. Lines in Decennial Subject Indexes of Chemical Abstracts

	Lines	Cumulative total
1907–16	3.6×10^5	3.6×10^5
1917–26	6.2	9.8
1927–36	15	24.8
1937–46	20	44.8
1947–56	43[a]	87.8

[a] Estimate based on annual indexes, corrected for a 17% reduction in number of lines when annual indexes are combined into decennial indexes.

Table 2. Cumulative Subject Index Lines in Chemical Abstracts

Year	Lines	Year	Lines
1906	8×10^5	1936	32.8×10^5
1916	11.6	1946	52.8
1926	17.8	1956	95.8

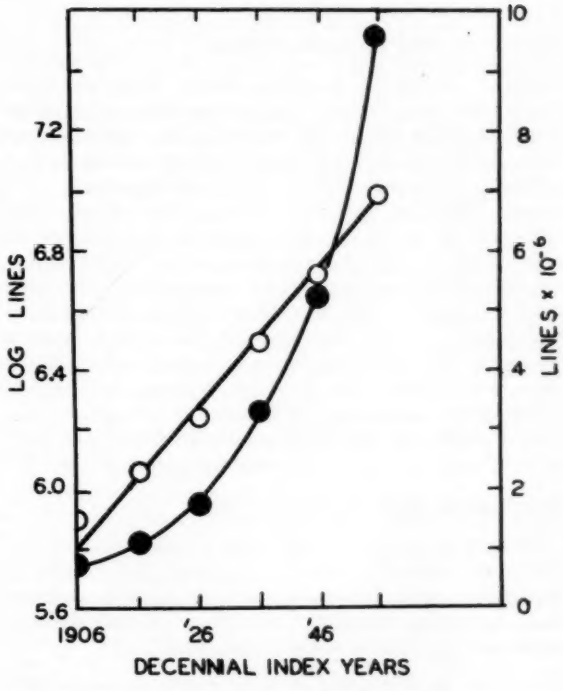

Figure 1. *Chemical Abstracts* cumulative lines in indexes.

From the logarithmic plot it appears that during the past half century the amount of chemical information has approximately doubled each thirteen years.[2] Of course the sobering implication of this is that in the period from now until 1973 an amount of chemical information will be published equal in magnitude to all that has been published in the past.

Other Growth Patterns in Science

A similar rate of growth to the one just mentioned is that reported for the Library of the London Chemical Society. When the library was founded in 1841, a single bookstack sufficed. In 1900 the library contained 10,000 volumes and in 1918 its holdings amounted to 25,000.[3]

Other aspects of science in addition to chemistry show somewhat similar expansion patterns. In Figure 2 are plotted two different indexes of this growth. The left hand line describes the increase in number of names published in successive volumes of "American Men of

[1] Strong, L. E., and Benfey, O. T., J. Chem. Educ., **35**, 164 (1958).

[2] This estimate is also supported by the fact that the second supplement (1920–29) to Beilstein is approximately twice as large as the first (1910–19).

[3] Anon., *Proc. Chem. Soc.*, 226 (1957).

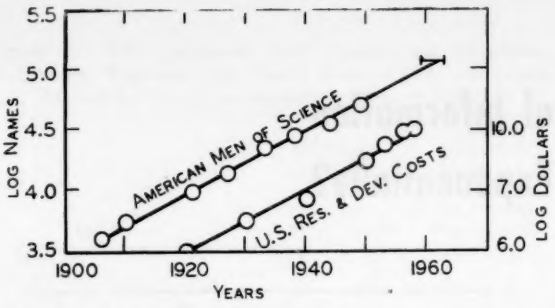

Figure 2. Growth in some aspects of science.

Science" during the past fifty years.[4] The right hand line shows total expenditures for research and development made in the United States during various years since 1920.[5] Each set of data conforms reasonably to a straight line when plotted semi-logarithmically. For names listed in "American Men of Science" the best straight line has a slope corresponding to doubling each twelve years while for research and development expenditures the line has a slope corresponding to doubling each six years. That research and development money increases so much more rapidly than publication is probably not surprising since a large fraction of the money in recent years goes into military work where publication and similar public activity are greatly curtailed. Thus in 1957–58 it is estimated that over 55% of total expenditure was for military purposes.

Parabolic or Exponential?

It may be that the phenomenon under discussion is not even limited to science. Fremont Rider, after an exhaustive study of the growth of American college and university libraries, finds that, on the average their holdings double every sixteen years:

> To be sure the tables cited carry the story back only to 1831; but every scrap of statistical evidence that we can gather shows that as far back as we can reach, the story is exactly the same. It seems, as stated, to be a mathematical fact that, ever since college and university libraries started in this country, they have, on the average, doubled in size every sixteen years.[6]

Our calculations lead us to believe that the growth of chemical information is more rapid than the rate suggested recently by Crane.[7] Crane predicts, on the basis of the number of abstracts published in *Chemical Abstracts* during the last ten years, that the number of abstracts published per year will increase linearly during the next years. This implies a quadratic or parabolic growth curve for the *total* number of abstracts whereas a doubling of information implies a logarithmic growth curve. While over a short period of a few years, the difference between the two functions is small, in a period of ten years or more the difference rapidly becomes quite large. Of course an exponential function implies that cumulative knowledge approaches infinity as a limit, an event which is certainly to be avoided if at all possible.

While it seems clear that the accumulation of chemical information in the past has approximated an exponential curve there is no theory for this relation. Consequently one cannot make a prediction about the future with any great confidence. The implication of an exponential increase is most distressing since it implies a staggering amount of publication for the not very distant future. How can even a modest fraction of this be assimilated?

A few years ago, Alan Gregg published a provocative article on the population problem.[8] He suggested that the expansion of the human population of the earth has certain similarities to the growth of a cancerous tumor in a living organism. At worst this is no more than an interesting analogy but Gregg points out, "To say that the world has cancer, and that the cancer cell is man, has neither experimental proof nor the validation of predictive accuracy; but I see no reason that instantly forbids such speculation."

Probably we should hope that the exponential relation presented here and the parabolic relation suggested by Crane are both wide of the mark. It would be comforting to know that we are dealing with an S-shaped growth curve which leads to an essentially constant annual publication rate. Lacking this comfortable assurance perhaps we need to explore the possibility that chemistry is in danger of growing in a cancerous and indigestible way.

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[4] CATTELL, J., AND J. MCK., *editors*, "American Men of Science," Science Press, Lancaster, Pa., 5th ed., **1933**, p. vii; 6th ed., **1938**, p. viii; 7th ed., **1944**, p. v; 8th ed., **1949**, p. i; 9th ed., **1955**, Vol. I, p. i; Vol. III, p. i; publisher's announcement of the 10th edition, **1959**. The ninth and tenth editions include a fuller coverage of the social sciences.

[5] *Chem. Eng. News*, **36**, 63–9 (1958).

[6] RIDER, F., "The Scholar and the Future of the Research Library," Hadham Press, New York, **1944**, p. 8.

[7] CRANE, E. J., *Proc. Chem. Soc.*, 334 (**1957**).

[8] GREGG, A., *Science*, **121**, 681 (1955).

Chemical Industry Facts Book 1960–61 Edition

The Manufacturing Chemists' Association announces the availability of the new fourth edition of its popular Facts Book, first published in 1953. New chapters on food, shelter, and space accompany the complete revision of former sections. The book reflects the latest information, much of it conveniently summarized from government reports on what the chemical industry is and does.

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Bernard Krabacher, Lawrence Kirch, and **Milton Orchin**
University of Cincinnati
Cincinnati, Ohio

Reaction Rates at High Pressures

The oxo reaction

The increasing use of high pressure reactions and the increasing need for securing quantitative data for mechanism studies has led to the inclusion of high pressure rate experiments in the course on techniques of chemistry given at the University of Cincinnati during the summer months. The present paper describes the apparatus, procedure, and results of an experiment on the Oxo reaction.

The Oxo reaction[1,2] consists of the conversion of an olefin to an aldehyde by treatment of the olefin with a mixture of carbon monoxide and hydrogen at elevated temperatures and pressures in the presence of a cobalt catalyst:

$$R{-}CH{=}CH_2 + CO + H_2 \xrightarrow[110\text{–}180^\circ]{2500\text{–}4500\ \text{psi}} R{-}CH_2CH_2CHO \qquad (1)$$

Although it probably does not proceed by such a process, the reaction may be visualized as consisting of the addition of H— and —C(=O)H across the double bond of the olefin and accordingly is frequently called the hydroformylation reaction. In equation (1) the reaction is written to show that the formyl group has added to the terminal carbon atom and the hydrogen to the penultimate carbon. However, the branched chain aldehyde is also secured and this may be formally rationalized on the basis of reverse addition whereby the hydrogen adds to the terminal carbon and the formyl group to the internal carbon atom. Almost any compound of cobalt, and even metallic cobalt, catalyzes the reaction. In practice, dicobalt octacarbonyl $Co_2(CO)_8$[3] or cobalt naphthenate, both of which are soluble in organic solvents, are used as catalysts. Under the reaction conditions the cobalt compounds are readily converted to cobalt hydrocarbonyl, $HCo(CO)_4$, which is thought to be the true catalyst.[4]

A schematic diagram of the apparatus is shown in Figure 1. Such an arrangement is fairly common. Blowout discs are provided above the compression cylinder and on the autoclave. The autoclave is installed behind a well-ventilated barricade. A carbon monoxide alarm is placed near the autoclave but outside the barricade. Heat control and temperature recording devices are not shown. These are arranged so that it is not necessary to enter the barricade when the autoclave is hot. A cross is provided for the addition of further autoclaves to the system.

The autoclave is charged with olefin, dicobalt octacarbonyl, and solvent. In no case should the total volume of the charge exceed 40% of the total volume of the autoclave. The autoclave is sealed and placed in its heating jacket. The following flushing and filling procedure is employed.

Procedure for Flushing and Filling the Autoclave (See Fig. 1)

Preliminary Check of the Equipment. Close all the valves in the high pressure system. Check gauge G-4 to be sure that the gas compression cylinder does not contain any high pressure gases. If gauge G-4 indicates pressure, vent the gases by opening valves 5 and 7. Close valves 5 and 7.

Flushing the Autoclave with Nitrogen. Open the valve on the nitrogen cylinder and open valves 1, 4, and 5 until gauge 4 indicates a pressure of 500 psi. Close valve 4. Vent by opening valve 7 until gauge G-4 still indicates a slight pressure. Close valve 7. Repeat this procedure two times.

Add nitrogen to the autoclave by opening valves 4, 8, and 9 and when gauge G-6 indicates 500 psi, close valve 9. Vent the gases slowly by carefully opening valves 10 and 11. Close valves 10 and 11. Repeat this step two times.

Close the valve on the nitrogen cylinder and close valve 1. Vent the gas in the compression cylinder by opening valve 7 until gauge G-4 still indicates a slight pressure. Close all remaining valves.

Pressuring the Autoclave with Carbon Monoxide. Open the valve on the carbon monoxide cylinder and open valves 3 and 4 to fill the compression cylinder. Force the oil from the compression cylinder into the reservoir by opening valve 6. When the level of the oil in the sight glass indicates 1500 ml, close valve 6.

Add carbon monoxide at cylinder pressure to the autoclave by opening valves 5, 8, and 9. Close the valve on the carbon monoxide cylinder and close valves 3 and 4. At this point only valves 5, 8, and 9 should be open; be sure all other valves are closed.

Start the compression pump. Gauges G-4, G-5, and G-6 should read the same pressure. Check the readings of these gauges periodically during the pumping period. The oil level in the sight glass should also be checked. At no time allow the oil to fall below the danger level (200 ml). If the oil does fall to the danger level stop the pump at once. When the pressure reaches 1300 psi stop the pump. Close valve 9.

Vent the gas in the compression cylinder and in the lines by opening valve 7 until gauge G-4 still indicates a slight pressure. Close valves 7 and 5.

Pressuring the Autoclave with Hydrogen. Fill the compression cylinder with hydrogen by opening the valve on the hydrogen cylinder and by opening valves 2 and 4. Force the oil from the compression cylinder into the reservoir by opening valve 6. When the level of the oil in the sight glass reaches 1500 ml, close valve 6. Close the valve on the hydrogen cylinder and close valves 2 and 4. At this point all valves but valve 8 are closed.

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[1] Orchin, M., and Wender, I., Encyclopedia of Chemical Technology, Vol. 9, p. 699, Interscience Encyclopedia, Inc., New York, 1952.

[2] Orchin, M., "Unit Processes in Organic Syntheses," Groggins, P. H., *editor*, McGraw-Hill Book Co., Inc., New York, 1952, p. 589.

[3] Wender, I., Sternberg, H. W., Metlin, S., and Orchin, M., "Inorganic Syntheses," Vol. 5, McGraw-Hill Book Co., Inc., New York, 1957.

[4] Orchin, M., Kirch, L., and Goldfarb, I., *J. Am. Chem. Soc.*, **78**, 5450 (1956).

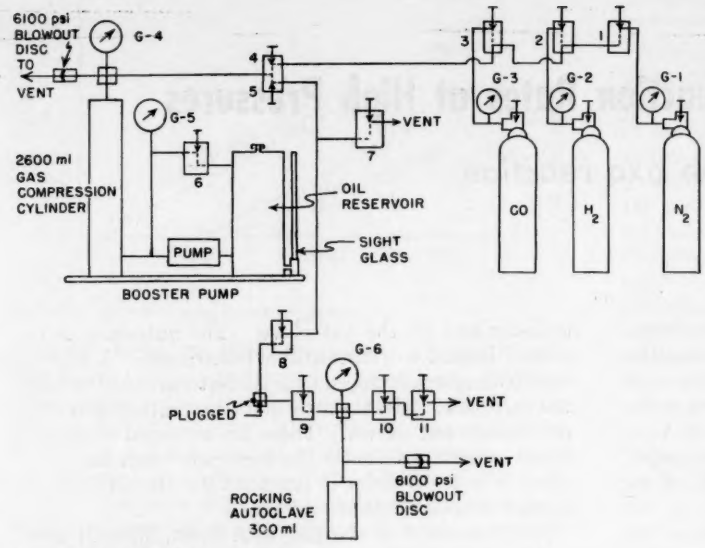

Figure 1. Schematic diagram of high pressure system.

Start the compression pump. Check the level of the oil in the sight glass periodically. At no time should the level fall below the danger level (200 ml). If the oil does fall to the danger level, stop the pump at once. When the pressure reaches 4000 psi as indicated by gauge G-4, stop the pump.

Open valve 5. Admit the hydrogen into the autoclave by opening valve 9. When the pressure as indicated by gauge G-6 reaches twice the carbon monoxide pressure, close valve 9.

Vent the gases in the compression cylinder by opening valve 7. When gauge G-4 indicates zero, close all valves.

Calculations and Results

Since the oxo reaction is first order with respect to olefin it should be first order with respect to gas absorption, and accordingly it is appropriate to employ the standard integrated first order rate expression,

$$kt = \ln \frac{a}{a - x} \qquad (2)$$

where x is the number of moles of compound which have reacted in time t, and a is the initial concentration. If the initial pressure in the system at reaction temperature is denoted as P_i and the final pressure at reaction temperature after reaction is complete and 2 moles of gas per mole of olefin (or 4 moles of gas per mole of diolefin) have been absorbed is denoted as P_f, then the initial concentration of olefin, a, is proportional to $P_i - P_f$. If the pressure at any time, t, is denoted by P_t, then the amount of olefin which has reacted in time, t, is x and is proportional to $P_i - P_t$. Since $a = P_i - P_f$ and $x = P_i - P_t$, $(a - x) = P_i - P_f - P_i + P_t = P_t - P_f$ and substitution into (2) gives

$$kt = \ln \frac{P_i - P_f}{P_t - P_f} \qquad (3)$$

and

$$2.3 \log (P_i - P_f) = -kt + 2.3 \log (P_i - P_f) \qquad (4)$$

The plot of this equation gives the rate constant in the usual manner. Ordinarily the rate of a reaction in which gas is absorbed would be expected to decrease with decreasing pressure, but the rate of the oxo reaction is affected equally but in opposite directions by the partial pressure of hydrogen and carbon monoxide and so the rate is approximately independent of total pressure.

The volume of the autoclave and system to the valves 9 and 10 (Fig. 1) was calibrated by hydrogenating a known quantity of acetone. The volume was found to be 360 ml. From the measured amount of solution containing a known weight of olefin, the free space in the autoclave and the calculated pressure drop are readily secured from which P_f is calculated. The value of P_f in the experiment below is 720 psi.

In these experiments the olefin employed was a mixture of octadienes prepared from the dimerization of butadiene in a process developed by U. S. Industrial Chemicals Company laboratories in Cincinnati. The mixture was reported to be straight chain material with the double bonds at either the end position or the 2-positions.

In a typical experiment, 50 ml of octadiene (0.350 mole) and 44 ml of a solution of $Co_2(CO)_8$ in hexane (0.014 mole or 4.0 mole per cent octacarbonyl) were sealed in the autoclave. In accordance with the procedure described above, the autoclave was charged with carbon monoxide, the heat was turned on, and after the temperature reached 122° and was steady, hydrogen was introduced to twice the carbon monoxide pressure. In this particular experiment, the pressure at zero time was 3200 psi. The pressure was read at short intervals during the first hour and at longer intervals thereafter. After 205 min, the heat was turned off, and the pressure at this time was 1260 psi. When a log plot is made of these data in accordance with equation (4), the points can be connected by two separate straight lines with obviously differing slopes (Fig. 2). It will be noted that there appears to be an abrupt change of rate at about 70 minutes (intersection of line) at which time the reaction was approximately 70% complete. Without any further careful analysis of the data, it can be assumed for present purposes that the two different rates result from hydroformylation at two different kinds of double bonds, the terminal double bonds, and the internal double bonds (which react much more slowly). The observed rate

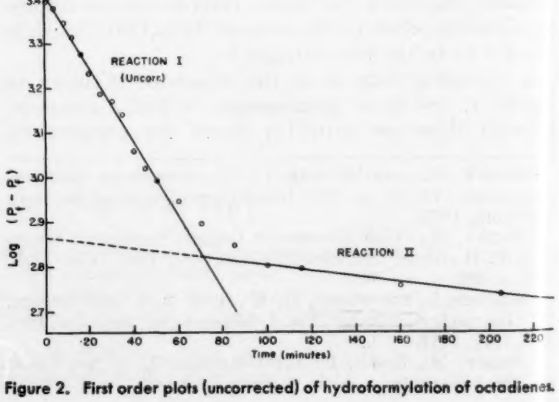

Figure 2. First order plots (uncorrected) of hydroformylation of octadienes.

during the first part of the reaction is the result of two different reactions proceeding simultaneously, but the final or slow reaction can be assumed to result from attack at only internal double bonds.

To obtain a true reaction rate for the first or fast part of the reaction, a correction for the slow rate must be made. This can be done by extrapolating the lower rate curve (reaction II) back to zero time and making the appropriate correction in the upper curve according to the procedure employed in treating rate data in systems where two or more reactions are proceeding simultaneously, as for example, radioactive decay systems.[5] The rate constant for reaction I (corrected) as calculated from Figure 3 and equation (4) is 34.9×10^{-3} min^{-1}, and the rate constant for reaction II as calculated from Figure 2 and equation (4) is 1.5×10^{-3} min^{-1}.

This particular example was chosen to be illustrative and may not represent the true rate difference between the hydroformylation of the two kinds of double bonds in the octadiene. The simplifying assumption was made that only two kinds of double bonds are present; furthermore these particular data represent data for only one experiment.

Acknowledgment

The authors wish to thank Drs. Frampton and Feldman for suggesting the treatment of the rate data.

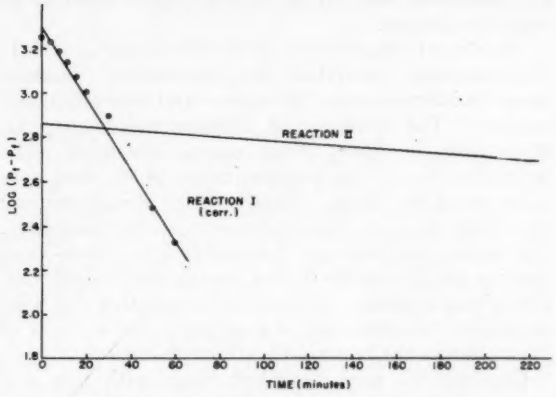

Figure 3. First order plots (corrected) of hydroformylation of octadienes.

[5] Friedlander, G., and Kennedy, J. W., "Nuclear and Radiochemistry," John Wiley and Sons, New York, 1955, p. 128.

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South Dakota State College
Brookings

A Topical Approach to Organic Chemistry for Agricultural Students

Students majoring in the various agricultural departments are generally required to take at least one course in organic chemistry. At South Dakota State College all agricultural students are required to take a minimum of one year of inorganic chemistry and one quarter of organic chemistry.

The one quarter organic course consisting of three hours of lecture per week amounts to a total of some 35 class meetings. Besides the lectures, the class meets for biweekly laboratory sessions.

The classical approach to the service course is the presentation of the various types of organic compounds in appropriate sequence. For example, alkanes are generally introduced first followed by alkenes, alkynes, halides, alcohols, etc. Each of these topics include nomenclature, properties, reactions, and often applications. The textbooks published for these short courses, in general, follow this classical outline.

Deviations from this classical approach have been carried out in an attempt to rectify a common student complaint: "We can see no use in learning a lot of organic chemistry for the type of work we will be doing." Moreover the short course, by cramming a large number of facts into a short period paying little attention to the relative importance or pertinence to the particular interests of the student, makes retention of the essentials difficult. The topical approach has successfully solved the first of these difficulties in that student interest and morale is much higher than that encountered when the course is taught by a classical approach. Whether retention is any greater remains to be seen over the next few years.

Presented before the Division of Chemical Education at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

Topics Considered

The topical approach involves the discussion of a series of topics of direct interest to those enrolled in the course. Along with each topic all principles necessary to instill a sufficient chemical background are thoroughly covered.

Ethyl alcohol was used as the introductory topic since it is a relatively simple compound widely known because of its presence in fermented beverages. It has also been in the news lately as an ingredient in cattle feeds to improve utilization of urea (*1*, *2*). The supporting, materials included a discussion of organic structures, structural representations, tetrahedral carbon atoms, and alcohol nomenclature. The latter was introduced

along with the various alcohols found in fusel oil. The tyrosol found in fusel oil was then used as a departure point for a discussion of sigma and pi bonds, resonance concepts, aromatic character, and acidity of phenols (*3*). Oxidation of alcohols was discussed in conjunction with the use of alcohol as the hydrogen donor in urea metabolism (*1*). Elimination to form olefins was discussed as a hypothetical method by which surplus farm crops might be utilized.

Chlorinated insecticides included Lindane, DDT, Methoxychlor, Chlorodane, and Heptachlor. Lindane served to introduce stereochemistry and conformational analysis. The synthesis of Lindane necessitated an explanation of ionic versus radical reactions. The details involved in the polymerization of ethylene were taken up at this point. Methoxychlor opened the way to the introduction of the rudiments of ether chemistry. Heptachlor and chlorodane introduced the Diels-Alder reaction and hence the further commercial insecticides, Dieldrin and Aldrin. Eliminations and other reactions of halides were discussed in relation to the stability of these chlorinated insecticides after application.

Vegetable oils were described along with fats and waxes. Ester and acid nomenclature, esterification and hydrolysis reactions, hydrogenation and autoxidation processes, and saponification and iodine numbers were presented in detail. Soaps and synthetic detergents led to a discussion of emulsifications and solubility problems in general.

Herbicides. Since soaps are often used in emulsifying herbicide preparations, a natural transition was made to herbicides. Besides the water emulsion of 2,4 D ester, the principles involved in dissolving 2,4 D amine salts and sodium salt of 2,4 D in water were discussed. Other herbicides such as TCA and 2,4,5 T were also mentioned. The reactions used in preparing these derivatives helped to point out more of the general principles involved in acid and acid derivative chemistry.

The *insecticides* TEPP, Parathion, and Malathion served as excellent examples of acid anhydrides and thio analogues of alcohols, esters, and acids.

Amino acids and proteins then served to completely round out acid and acid derivative chemistry.

The *natural product insecticides* such as pyrethrin, allethrin, rotenone, and Sabadilla, along with the synergists such as piperonyl butoxide and Sesoxane (*4*), are ideal compounds for use in illustrating multiple functional groups in complex compounds as well as the abbreviated structural representation commonly used with complex organic compounds.

Starch and cellulose pointed the way to monosaccharides and hence to carbonyl chemistry. Nomenclature and reactions of carbonyl were presented with a particular emphasis on hemiacetal and acetal chemistry. This subject also led to a review of stereochemistry taken up earlier in the course.

In general, the course presented in this topical manner contains much of the material found in a standard short course in organic chemistry. It can be seen that the omissions are for the most part reactions of primary interest in synthetic organic chemistry. On the other hand, a selected number of reactions which are necessary for the understanding of the chemistry of the compounds discussed is very carefully considered. Simplified reaction mechanisms are presented (*3*). This is done with the aim of conveying a sense of the bond forming and bond breaking processes involved in organic reactions rather than indoctrinating the student with an arbitrary list of organic reactions.

There is a problem in assigning a text for a course presented in this manner. Since no text available presents material in the particular sequence employed, students in any case will have to read selectively. A satisfactory solution is a standard text with a mimeographed reading guide pointing out sections where the appropriate background material can be located.

The author will be glad to supply this to interested readers or to discuss in more detail the topics under which the conventional elementary organic materials are discussed.

A laboratory which correlates with the lectures has not yet been developed. Two approaches have been tried thus far. One emphasized familiarity with organic compounds through the "reactions and properties of" type of experiment. The other was a project type of laboratory in which some of the compounds discussed in the lecture were synthesized or extracted. At the present time the latter seems to show more promise of developing into a good supporting laboratory for the lecture part of the course.

The topical approach introduces each of the major types of organic compounds along with a sampling of the chemistry of each. The students generally expressed approval of the course in unsigned criticism sheets returned at the end of the quarter. It is hoped that some of the concepts of organic chemistry will be retained longer by better motivated students.

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The National Science Foundation estimates total funds for scientific research and development in the United States will reach an all-time high of $12 billion for the year 1959–60, up $7 billion from the level of 1953.

A Foundation study, "Funds for Research and Development in the United States, 1953–59," found an increase of nearly 160 per cent in funds used in the performance of R&D by private firms and related organizations from 1953–4 to 1959-60. More than half the funds expended by industry were found to have come from the Federal Government, with 70 per cent of industry's funds expended on development rather than research.

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Vapor Pressure Determination

An elementary experiment

The approximate vapor pressure of low boiling liquids, such as benzene, chloroform, ethyl acetate, and carbon tetrachloride may be estimated by measuring the increase in length of an air column trapped between two short columns of mercury in a uniform diameter glass tube, when the liquid vaporizes between them. As Damerell[2] has pointed out, the volume in such cases is proportional to the length of the gas column when the length of the column is considerably greater than its cross section.

The apparatus consists of a meter stick, several medicine droppers which have been drawn out into capillary pipets, a small rubber bulb with a hole in each end, a few milliliters of mercury, and a piece of constant bore glass tubing about a meter long and 1 or 2 mm i.d. The tubing may be tested for uniformity of bore by measuring the distance between two short mercury globules about 20 cm apart as they are drawn up and down the tube by means of the rubber bulb. The tubing may be bent a few centimeters from the end, to facilitate manipulation and prevent it from accidentally rolling off the table.

The experiment is performed by introducing a short column of mercury, about 1 cm long, into the measuring tube by means of one of the capillary pipets. The mercury is drawn down the tube by means of the rubber bulb attached to the opposite end until an air column about 40 cm long has entered the tube. Another short column of mercury is then introduced to serve as a seal. The mercury globules are drawn into the central portion of the tube and the distance between them is measured to the nearest millimeter with the meter stick. The mercury globule nearest the open end of the tube is forced to within a few millimeters of the end of the tube and a short column of the liquid is drawn into the tube behind the mercury. As the organic liquid is drawn into the tube it wets the glass. Reversal of the direction of flow causes the mercury globule to roll over a film of this liquid, thus introducing the sample into the space between the mercury globules. The amount of liquid between the globules may be increased by rolling them back and forth a few times. It is necessary that a small excess of liquid be present after equilibrium has been reached, but a considerable excess is not desirable. After introduction of the sample the tube is allowed to stand until equilibrium has been reached as evidenced by constancy of length of the air column on standing, the globules are drawn into the part of the tube where the original measurement was made, and the length of the air-plus-vapor column is measured.

Attainment of equilibrium may be accelerated by closing the open end of the tube with a medicine dropper bulb in such a way that the mercury remains at least 30 cm from the opposite end of the tube and turning the tube so that its axis is vertical with the organic liquid at the upper end. If the tube is stroked between the thumb and forefinger in the vicinity of the upper mercury globule, the temperature in this region will be elevated, causing the liquid to evaporate more rapidly, and the dense vapors to move more rapidly down the tube axis. The tube may then be returned to its horizontal position and allowed to stand for five minutes to establish thermal equilibrium with the atmosphere; and a measurement of the length of the air column is recorded. This process may be repeated until a constant length of air column is obtained.

The barometer reading, temperature, original and final lengths of the air column, and the identity of the liquid should be recorded. The tube is then emptied and thoroughly flushed with dry air to remove all traces of the organic liquid. Vapor pressure determinations at different temperatures may be made by putting a small condenser jacket around the tube and circulating water of known temperature through it or preferably by repeating the experiment at another laboratory period when the temperature has changed or in a different room where the temperature is different. From data at two different temperatures an approximate heat of vaporization may be calculated for the liquid. If a suitable long tube is available it is possible to conduct duplicate determinations simultaneously by introducing a column of mercury about 2 cm long between the outside mercury columns, thus forming 2 air columns each of which can be charged with sample from its end of the tube. If this is attempted, each outer mercury globule must be brought to rest at least 25 cm from the end of the tube prior to equilibration so that it is not ejected from the tube during vaporization.

The vapor pressure is given by the equation:

$$P_v = P_B \times \frac{(L_1 - L_2)}{L_2}$$

P_v = vapor pressure of the liquid
P_B = barometric pressure
L_1 = length of air column
L_2 = length of air-plus-vapor column

Typical results for the vapor pressure of chloroform (30°C), measured by this method were 246 mm, 252 mm, and 250 mm. Refinements such as calibrated uniform bore tubing and careful temperature control should make the method capable of high precision.

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Density Measurements with a Magnetically Controlled Float

In 1913 Lamb and Lee (*1*) reported the first use of a magnetically controlled float to determine liquid densities. For a number of salt solutions they obtained densities with a probable error of less than one part in 10^7. Although other investigators (*2, 3, 4, 5, 6*) have since employed the method, it has not become a common one. We feel that its simplicity, high sensitivity, and modest cost recommend it for student use. With this in mind we later describe several determinations which illustrate the versatility of the magnetic float and are suitable as laboratory exercises in the undergraduate physical chemistry course. The student can acquire useful experience during the construction and calibration of the necessary apparatus.

Theory and Calibration of Float

The method is quite simple in principle. A glass float containing a small magnet or piece of soft iron is completely immersed in the liquid whose density is to be measured. The liquid and float are contained in a glass cell in a thermostat. A force downward on the float is exerted by the magnetic field produced by a solenoid located underneath the cell. For a given position of the float this force is assumed to be proportional to its volume and to the difference in density between the float and its surroundings. When the two forces are in balance

$$ki = gV_f(d - d_f) \tag{1}$$

where

k = force per unit current exerted on the float by the magnetic field
i = current in solenoid
g = acceleration of gravity
V_f = volume of float
d = density of liquid
d_f = density of float

Upon rearrangement of (1) we obtain

$$d = \frac{k}{gV_f} i + d_f \tag{2}$$

The density is thus a linear function of the current. The constants in (2), k/gV_f and d_f, can be determined conveniently by measuring equilibrium currents for several solutions whose densities are known.

Occasionally it may be necessary to work with liquids whose densities differ enough from the float density so that currents too large for the source, solenoid, or galvanometer will be required to operate the float. This situation can be handled in at least two ways. A new float with a higher density can be constructed or weights can be added to the float on hand to increase its effective density. If the latter course is followed, densities are given by

$$d = \frac{k}{g(V_f + V_m)} i + \frac{V_f d_f + V_m d_m}{V_f + V_m} \tag{3}$$

where

V_m = volume of the added weights
d_m = density of the added weights

As in the case of the unweighted float, the liquid density is a linear function of the solenoid current. The constants, $k/g(V_f + V_m)$ and $(V_f d_f + V_m d_m)/(V_f + V_m)$, can likewise be determined by measuring equilibrium currents for liquids whose densities are known.

In some instances, such as with non-aqueous solutions, it may be difficult to obtain liquids with accurately known densities in the operating range of the float. In other instances, it may be necessary to use the float over an extended density range for which no single added weight will suffice. For these situations, a calibration can be made—provided the mass and the volume of the float have been determined previously—by measuring the change in equilibrium current caused by the successive addition of weights of known mass to the float operating in a liquid of known density.

The equilibrium current can be expressed as a function of the added mass. Thus on rearrangement of (3) one finds

$$i = \frac{g}{k}\left[\frac{d_r}{d_m} - 1\right] M + \frac{g(d_r V_f - M_f)}{k} \tag{4}$$

where

d_r = known density of liquid in cell
M = total mass of the weights added to the float
M_f = mass of float

A plot of i versus M will give a straight line whose slope and intercept may be used to obtain the calibration constant of the float. Thus

$$\frac{k}{g} = \frac{d_r V_f - M_f}{i_r} \text{ and } d_m = \frac{d_r}{1 + (ks/g)}$$

where

i_r = intercept of the current axis
s = slope

Once k/g and d_m are known, the constants in (3) can be evaluated for any fixed weight on the float.

If one uses a large float with a density close to those of the liquids being examined, small weights and small currents will be sufficient to operate the float. If the weights are made of a material whose density is

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high compared to that of the float and if no more than a small density range is to be explored, liquid densities may be computed from

$$d = d_f + aM + bi \qquad (5)$$

The determination of d_f, a, and b will be described later.

Description and Operation of a Simple Apparatus

The pertinent components of the apparatus are sketched in Figure 1. Water in the thermostat is heated by an infrared lamp and continuously circulated by an external pump. According to the manufacturer, the thermostat is capable of maintaining a temperature to ± 0.002°C.

The watertight aluminum box containing the solenoid is held in place by brass tubes bolted to a wooden support which is notched to rest firmly on the top of the bath. The solenoid is a 170-ohm coil salvaged from a junk box. The Pyrex cell is approximately 100 ml in capacity. It is held in position by a metal ring on the solenoid box and a notch in the support.

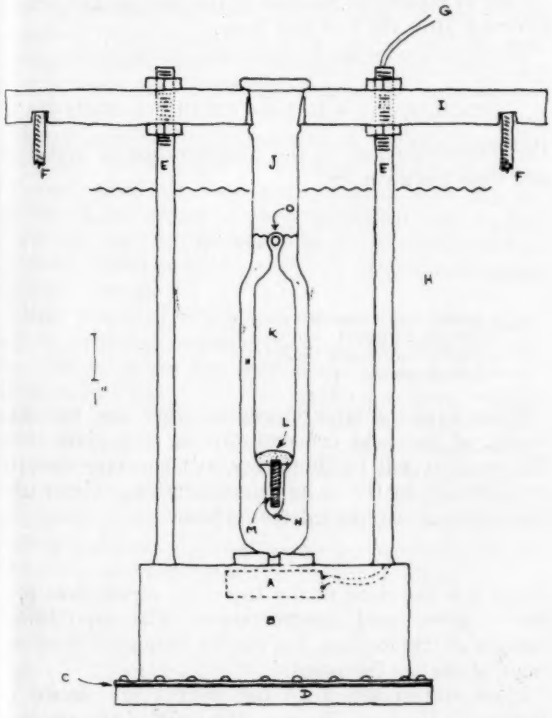

Figure 1. Sketch of magnetic float, cell, and cell holder. *A*—solenoid, *B*—solenoid box, *C*—gasket, *D*—cover plate, *E*—brass tubes, *F*—thermostat wall, *G*—solenoid leads, *H*—bath, *I*—wooden support, *J*—cell, *K*—float, *L*—mercury, *M*—magnet, *N*—cement, *O*—handling ring.

The floats are constructed from Pyrex tubing. They contain permanent magnets, cylindrical in shape and similar to those used in magnetic stirrer bars. Crude adjustments of float densities are made by the addition of mercury before sealing. Final adjustments are made by varying the amounts of glass on the handling rings (used to lower floats into or retrieve floats from cell by means of a hooked wire) until flotation is just possible in the liquid of interest with the lowest density. For the examination of liquids of greater density, platinum loops of various masses are slipped over the handling rings. A typical float has a volume of 37 ml and a k/gV_f of 1.55×10^{-4} $\Delta d/ma$.

The current supply for the solenoid consists of four "D" flashlight cells connected in series with a 5000-ohm helical potentiometer. Two relatively inexpensive potentiometers can be used in its place but not without some sacrifice of convenience. A push button switch is present in the circuit to make it possible to short out the potentiometer when a momentary current large enough to pull the float into position at the bottom of the cell is desired. The solenoid current is measured with an accurate milliammeter.

The apparatus is operated as follows. After the cell and its contents have come to temperature equilibrium, the solenoid current is increased to a maximum with the potentiometer in the circuit. The float is then pulled down to the bottom of the cell by depressing the push button momentarily. The current is next decreased rapidly until the float breaks free. This process gives the approximate "break-away" or equilibrium current. The solenoid current is then increased by a small amount and the push button depressed. When the float is again in position at the bottom of the cell, the push button is released and the solenoid current is reduced slowly until the float just breaks free. The milliammeter reading is recorded and the procedure repeated to check reproducibility.

The constants of equation (5) can be determined as follows. The float and a weighed amount of water sufficient to cover it are placed in the cell. After the break-away current has been measured, small increments of a concentrated solution of NaCl in water are added successively to the cell from a weight pipet, the break-away current being measured after each addition. When the amount of added NaCl is such that the range of the float is exceeded (break-away current too great to be read on the milliammeter scale), a platinum weight of known mass is placed on the float and the process of adding small weighed increments of the concentrated NaCl solution to the solution in the cell and measuring the resultant break-away currents is continued. The density of each successive solution in the cell is computed from its known composition and published NaCl-H_2O density data (*7*). All weighings involved in the calibration are corrected for atmospheric buoyancy.

A plot of solution density versus break-away current is made for each run with a fixed weight on the float. The slopes of these plots will be essentially the same and equal to the b of equation (5). Each density axis intercept represents the effective density of the combined float and added weights used in the run, i.e., $d_f + aM$. A plot of effective density versus M is then made. The intercept of this plot is the density of the unweighted float, d_f, and the slope is the a of equation (5).

Some Determinations Utilizing the Magnetic Float

With the apparatus described we have determined the critical micelle concentration of a surfactant, the rate constant of a reaction, the end points of several

titrations, and the partial molal volume of a component of a mixture. The procedures we followed will be described briefly now.

Critical Micelle Concentration of Dodecylammonium Chloride

At low concentrations surfactants exist in solution primarily as simple ions. At higher concentrations they may be present chiefly as ionic aggregates called micelles. The concentration above which any added surfactant appears in solution primarily in micellar form is termed the critical micelle concentration (CMC). The plot of almost any physical property of a surfactant solution against the surfactant concentration shows a break at the CMC. Addition of an inorganic salt lowers the CMC.

The apparatus of Figure 1 was used to determine, at 30°C, the CMC of dodecylammonium chloride in water and in 0.05 *M* NaCl. The surfactant was prepared by the method of Ralston and co-workers (*8*). In the first run, 1.0-ml increments of a 0.2091 *M* solution of dodecylammonium chloride were added successively to 80.0 ml of water contained in the cell. In the second run, the stock solution was 0.1045 *M* in surfactant and 0.05 *M* in NaCl. 1.0-ml increments of this solution were added to 80.0 ml of 0.05 *M* NaCl in the cell. The stock solutions were kept in the thermostat between pipettings to minimize the time needed for the establishment of thermal equilibrium.

After each addition of stock solution, the mixture in the cell was agitated by movement of the float. A wire hooked through the handling ring of the float was used to do this. A small error was introduced by this procedure since some of the cell contents were removed when the wire was withdrawn. For our purposes this error was of no great consequence.

Equilibrium current versus surfactant concentration plots for the two runs are given in Figure 2.

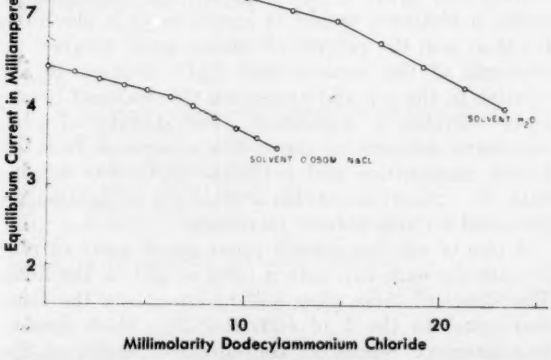

Figure 2. Determination of critical micelle concentrations of dodecylammonium chloride in water and in 0.05 M NaCl.

It is worth mentioning at this point that many surfactants are strongly adsorbed on glass and that anomalous curvature of the current versus concentration plot may occur for this reason. Large fractions of the first amounts of surfactant added to the solvent in the cell will be adsorbed on the walls of the cell and on the float itself. As a result the concentration of the surfactant in solution will be less than that calculated. In the determination just described, both cell and float were allowed to stand in contact with a solution of the surfactant, rinsed with distilled water, and finally allowed to air-dry before use. This treatment minimized the adsorption of surfactant during the subsequent runs.

Rate Constant for the Acid Catalyzed Hydrolysis of Acetal

The dilatometric measurement of the rates of hydrolysis of acetal and similar compounds (*9*) is frequently assigned as a laboratory exercise in chemical kinetics (*10*). These reactions can be followed conveniently with the magnetic float. We have followed the hydrolysis of acetal at 25°C in 2.76×10^{-4} and 5.53×10^{-4} *M* HCl.

The empty cell with magnetic float, a small flask with freshly distilled acetal, and a volumetric flask containing 100 ml of an HCl solution were placed in the thermostat. After temperature equilibrium with the bath had been attained, 2.00 ml of acetal was pipetted into the volumetric flask and the time recorded. The contents were shaken until the acetal phase disappeared and then were poured into the cell. Breakaway currents and the corresponding times were recorded as rapidly as possible at the start and at longer intervals after the first half hour.

The reaction for the hydrolysis of acetal is:

$$CH_3CH(OC_2H_5)_2 + H_2O \xrightarrow{H^+} CH_3CHO + 2C_2H_5OH$$

For dilute solutions C, the concentration of acetal at any time t, is given by

$$C = C_0 \frac{(i - i_\infty)}{(i_0 - i_\infty)}$$

where

C_0 = initial acetal concentration
i = current at time t
i_∞ = current at infinite time
i_0 = initial current

Because of the large excess of water and the constancy of the acid concentration in any given run, the reaction will be first-order and the rate directly proportional to the acetal concentration. Hence the rate constant may be calculated from

$$k = -S$$

where S is the slope of the $\ln(i - i_\infty)$ versus time plot for a given acid concentration. The equilibrium current at infinite time, i_∞, can be estimated from the trend of the last few points.

Plots corresponding to our results are shown in Figure 3. Heating effects at the start of the reaction and loss of significant figures during the subtraction of similar equilibrium currents at the end are probably responsible for the failure of the first and last points to lie close to the line. The negative slopes of the two lines, 0.034 and 0.051 $min.^{-1}$, for the respective HCl concentrations of 2.76×10^{-4} and 5.53×10^{-4} *M* are in reasonable agreement with the results of Brønsted and Wynne-Jones (*9*) as corrected to 25°C with the data of Kilpatrick and Chase (*11*).

"Densiometric" Titrations

The difference in volume between the products and the

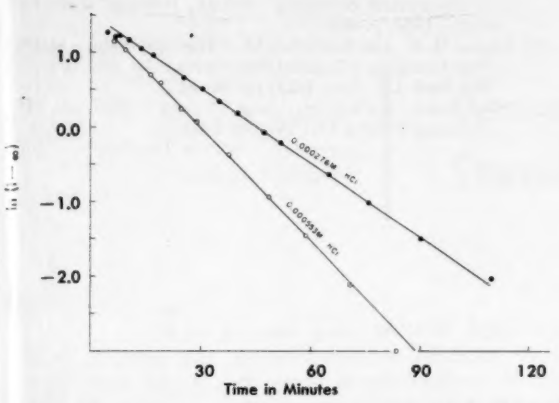

Figure 3. Determination of reaction rate constants for the hydrolysis of acetal in 2.76×10^{-4} and 5.53×10^{-4} M HCl.

reactants of a reaction can provide the means for finding the equivalence point. In an acid-base reaction, for example, the formation of water from hydrogen and hydroxyl ions is accompanied by a pronounced increase in volume (*12*). The end point of an acid-base titration should, therefore, coincide with a marked change of slope in the density versus titrant volume plot. If a magnetically controlled float is used to follow the density changes, a plot of solenoid current versus titrant volume will suffice to locate the equivalence point.

Figure 4 summarizes the results of two densiometric titrations. Seventy-five-ml portions of 0.101 *M* $HC_2H_3O_2$ and 0.097 *M* HCl were titrated with 2.1 *M* NaOH. A few drops of phenolphthalein were added to the cell in each titration to check the indicator end point (small vertical arrow) with the densiometric end point (break).

Other reactions which go virtually to completion may be followed densiometrically. For example, we were able to detect the equivalence point in the oxidation of Fe^{++} by Ce^{++++}. A 78-ml volume of 0.02 *M* $FeSO_4$ was titrated with 0.3 *M* $Ce(SO_4)_2$, both solutions being 1.1 *M* in H_2SO_4. A plot of break-away current versus volume of titrant gave two straight lines whose intersection marked the equivalence point. Unfortunately the two lines had nearly the same slopes which meant that the equivalence point could not be determined precisely without considerable effort.

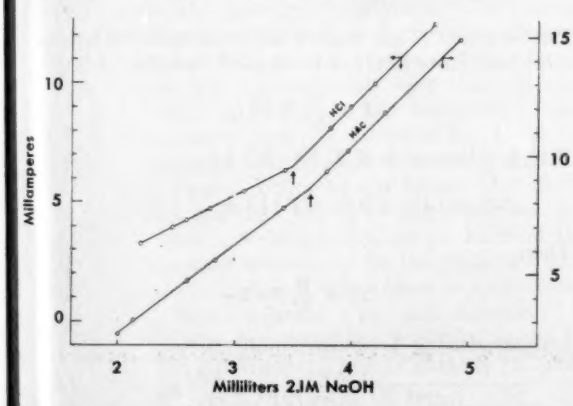

Figure 4. Determination of the equivalence points in the naturalizations of HCl and $HC_2H_3O_2$ with NaOH.

In its present state of development, the densiometric method of finding equivalence points has little or no advantage over the more conventional procedures. It is not likely to revolutionize analytical chemistry in the near future.

Partial Molar Volume of Sucrose

The partial molal volume of component i, $\bar{v}_i$, in a mixture is defined by

$$\bar{v}_i = \left(\frac{\partial V}{\partial N_i}\right)_{T,\,P,\,N_j}$$

where

V = volume of mixture
N_i = moles of component i in mixture
T = temperature
P = pressure
N_j = represents mole numbers of all components other than i in the mixture

The most obvious graphical method of determining $\bar{v}_i$ is to plot V versus N_i and take the slope of the resulting curve at any concentration as the value of $\bar{v}_i$ at that concentration. It should be remembered that all solutions must contain the same amounts of solvent and solutes (other than component i). Lewis and Randall (*13*) discuss a number of other methods for determining partial molal quantities.

The magnetic float can be used to determine partial molal volumes conveniently. We have tried to illustrate this with the sucrose-water system. Unlike the determinations previously described, a calibrated float must be employed.

Approximately 80 ml of water was weighed into the cell which was then placed in the thermostat set at 25°C. Small increments of a concentrated sucrose solution were then weighed successively into the cell from a weight pipet and the break-away current determined after each addition. The molality and density of each solution were then computed from the data. Finally, volumes of solution required to contain 1000 g of water were computed for the different mixtures and plotted against sucrose molality. The resulting curve was fairly linear up to the highest concentration examined, 0.06 *M*. Its slope was 212 ml/mole. The partial molal volume of sucrose in water computed from published density data (*14*) at 20°C is 210 ml/mole.

Acknowledgment

One of us, F. C., was in part supported by a grant from the Office of Ordnance Research.

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On the Boiling Point of a Dilute Solution

It is the purpose of the present paper to show how to derive Raoult's Laws, starting with Boltzmann's theorem and making no explicit use of the First and Second Laws of Thermodynamics. This approach will be found useful particularly when students have not gone through a detailed course on thermodynamics.

According to a known result of thermodynamics, the boiling point of a dilute solution of some nonvolatile solute is higher than that of the pure solvent. This difference is called the ebulloscopic raising and is given by

$$\Delta T = \frac{RT_0^2}{L_0} X_1 \tag{1}$$

where R is the gas constant, T_0 the solvent boiling point, L_0 its heat of evaporation, and X_1 the mol fraction of the solute.

We want to calculate the ebulloscopic raising through a reasoning of the statistical type. Let a liquid be in equilibrium with its vapor. If we call N_0 the total number of molecules, n^* the number of molecules that go from one phase to the other (dynamic equilibrium), E^* its kinetic energy, k the Boltzmann constant, and T the absolute temperature, we can define the probability for n^* molecules going in one direction or the other by

$$P_0 = \frac{n^*}{N_0} \tag{2}$$

At the boiling point this probability must reach some maximum value, M; then introducing the value of n^* given by the Boltzmann theorem

$$M = \frac{C_0}{N_0} e^{-E^*/RT_0} \tag{3}$$

where

$$C_0 = \frac{N_0}{\sum_s e^{-E_s/RT_0}}$$

If at the same time N_1 molecules of some nonvolatile solute are present, these formulas go to

$$P = \frac{n^*}{N_0 + N_1} \tag{4}$$

$$M = \frac{C}{N} e^{-E^*/RT} \tag{5}$$

where now this maximum M is reached at a higher temperature T, the boiling point of the mixture. (In passing from (3) to (5), it is permissible to keep the same E^*; why?)

After some manipulation, we get from (3) and (5)

$$\ln\left(\frac{N}{N_0} \times \frac{C_0}{C}\right) = \frac{E^*}{R} \times \frac{\Delta T}{T_0 T} \tag{6}$$

Let us calculate the relation N/N_0:

$$\frac{N}{N_0} = \frac{N_0 + N_1}{N_0} = 1 + \frac{N_1}{N_0} \backsimeq 1 + \frac{N_1}{N} \tag{7}$$

As $N_1 << N_0$, must be $N_1 << N$; then, in a good approximation

$$\ln \frac{N}{N_0} \backsimeq \ln\left(1 + \frac{N_1}{N}\right) \backsimeq \frac{N_1}{N} = X_1 \tag{8}$$

From (6) and (8)

$$\ln\left(\frac{N}{N_0} \times \frac{C_0}{C}\right) \backsimeq X_1 + \ln \frac{C_0}{C} \tag{9}$$

But because C/C_0 is tending to 1 as the solution becomes more and more dilute, equation (6) reduces to

$$\Delta T = \frac{R}{E^*} T_0 T X_1 \tag{10}$$

Which is the value of T_0T? We have

$$T_0 T = T_0(T_0 + \Delta T) = T_0^2\left(1 + \frac{\Delta T}{T_0}\right) \backsimeq T_0^2 \tag{11}$$

Then

$$\Delta T = \frac{R}{E^*} T_0^2 X_1 \tag{12}$$

and introducing Avogadro's number N_a

$$\Delta T = \frac{N_a R T_0^2}{N_a E^*} \times X_1 = \frac{RT_0^2}{L_0} X_1$$

which is formula (1).

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Demonstration:

Stress-Strain Behavior of Rubber

Two articles have recently appeared which describe the pressure-volume relations in a toy balloon along with some interpretations of the observed phenomena.[1,2] However, one intriguing aspect of the phenomena surrounding toy balloons, as a class, has thus far escaped discussion. We refer to the inflation characteristics of a cylindrical balloon.

When air is first introduced into a cylindrical balloon it expands evenly. That is, its circumference and length increase homogeneously in a manner consistent with the stresses imposed by the air pressure. Further addition of air causes a "bulge" to form while the remainder of the balloon retracts to dimensions which are somewhat smaller than they were just prior to the formation of the bulge. Inflation then continues through an elongation of the bulge until the entire balloon has been increased to the relative dimensions of the bulge. Still further inflation will proceed homogeneously again. There is a remarkable analogy between this manner of inflation and phase transitions such as boiling and freezing. This idea will be discussed in detail later in this article.

The cylindrical balloon imposes somewhat more of an experimental problem than does the spherical balloon. In order to analyze the response of the balloon throughout the course of its inflation, it is necessary to measure both circumference and length independently, and it is also desirable to be able to measure the "bulge" and "no bulge" phases separately. These conditions were met by using a photographic technique. Figure 1 shows the setup which was used. Pressure was introduced from an air compressor with regulation being obtained through a needle valve. The manometer fluid was sym-tetrabromo ethane (density 2.964) which was chosen to maximize the manometer sensitivity within the pressure range used. To increase the manometer readability, a red dye was dissolved in the manometer fluid prior to its use. With a movie camera, single frame photographs were taken at one-second intervals. After the film was developed, volume measurements were made, in arbitrary units, by the following technique: Individual frames of the film were projected onto a white sheet of paper; the outline of the balloon was then traced on the paper and approximated with a series of rectangles. Each of the rectangles was then assumed to be the projection of a right circular cylinder, and the volume was calculated accordingly. The pressure was also measured in arbitrary units directly from the projected image by measuring the difference in the heights of the fluid in the two legs of the manometer.

These measurements might have been made without resorting to photographic techniques by measuring the circumferences of the balloon with a dressmaker's tape and the lengths of the various segments with an ordinary ruler. While blessed with conceptual simplicity this latter method of measurement has its drawbacks. Balloon rubber has a certain amount of irrecoverable flow and retarded elastic response which imposes time dependence on the observed variables. The photographic method, on the other hand, permits the measurement of pressure-volume relationships right up to the bursting point under the conditions of constant influx of air. Several balloons were measured in this manner and a more or less complete picture of the stress-strain behavior was obtained.

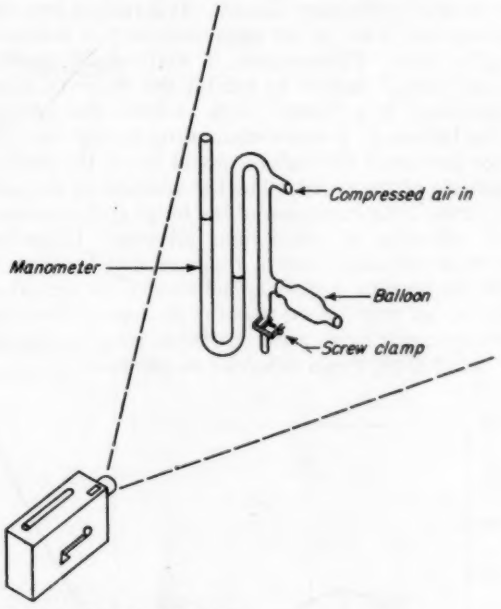

Figure 1. Experimental setup.

Let us now define an "ideal" cylinder as one in which the elastic response obeys the simple stress-strain relations as given by Treloar.[3] These two dimensional relations are:

$$\sigma_1 = G\left(\lambda_1^2 - \frac{1}{\lambda_1^2\lambda_2^2}\right)$$

$$\sigma_1 - \sigma_2 = G(\lambda_1^2 - \lambda_2^2)$$

where σ is the stress, λ is the extension ratio (i.e., the distance between two points in the strained state

[1] Stein, R. S., J. Chem. Educ., **35**, 203 (1958).
[2] Condon, F. E., and Fryd, M., J. Chem. Educ., **35**, 518 (1958).
[3] Treloar, L. R. G., "The Physics of Rubber Elasticity," Oxford University Press, New York, 1949.

divided by the distance between the same two points in the unstrained state), and G is a material constant. The subscripts 1 and 2 refer to the directions of principal stress which in the case of the cylindrical balloon would be denoted by t and l (tangential and longitudinal respectively).

From the above equations and the appropriate relations for the stresses in a cylinder under pressure, we can calculate the elastic response of our "ideal" cylinder. The stresses in a pressurized cylinder are:

$$\sigma_t = \frac{Pr}{d} = \frac{Pr_0}{d_0}\lambda_t^2\lambda_l$$

$$\sigma_l = \frac{Pr}{2d} = \frac{Pr_0}{2d_0}\lambda_t^2\lambda_l$$

where P is the pressure, r the cylinder radius, d the thickness of the cylinder wall, and the subscript 0 refers to measurements made in the unstrained state.

Figure 2 shows an "ideal" pressure-volume plot in comparison with observed data. It is readily seen that the two curves are in fair agreement only at relatively small strains. Furthermore, it would be impossible for an "ideal" balloon to exhibit the observed phase separation. If a "bulge" were to form, the pressure in the balloon as a whole would drop so that the non-bulge portion of the balloon would be on the positive slope side of the curve. Further addition of air could only result in an expansion of the bulge and a concomitant reduction of equilibrium pressure. Ultimately we would be faced with a bulge of infinite diameter while the remainder of the cylinder was in an unstrained state at an equilibrium pressure of zero. Therefore, it is once again necessary to postulate some mechanism for limiting the strain behavior of real balloons.[1]

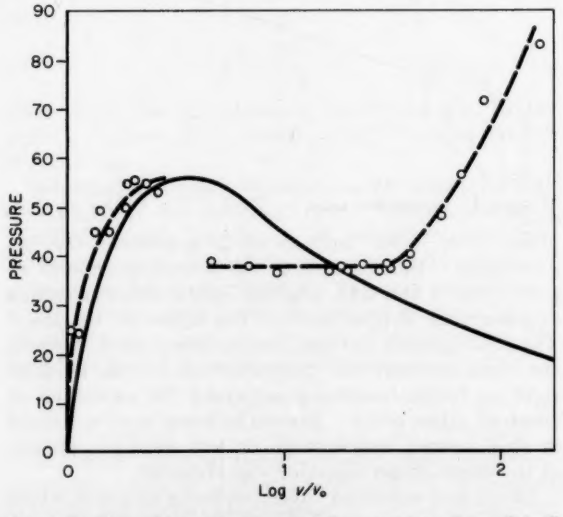

Figure 2. Comparison between calculated response of an "ideal" cylinder with observed values. The solid curve is the "ideal" response and the dashed curve is the experimentally observed response.

At the present time there is no truly satisfactory theory for the stress-strain behavior of rubber in the large strain region. This is particularly true in the case of arbitrary two- or three-dimensional strains. However, if we apply a one-dimensional theory to the observed phenomena we still have a reasonably plausible argument. James and Guth[4] arrived at a function which embodies the qualitative features of the stress-strain behavior of rubber by assuming a maximum extension available to the material. This function is the so-called inverse Langevin approximation and is given by:

$$\sigma = \frac{G}{3K}\left(\mathcal{L}^{-1}(K\lambda) - \frac{3K}{\lambda^3}\right)$$

where K is the reciprocal of the maximum possible extention ratio. The function $\mathcal{L}^{-1}(K\lambda)$ is obtained from the Langevin function $\mathcal{L}(\beta)$ as follows:

$$K\lambda = \mathcal{L}(\beta) = \coth\beta - 1/\beta$$

so that

$$\beta = \mathcal{L}^{-1}(K\lambda)$$

Figure 3 compares an inverse Langevin function, a Gaussian chain function, and the observed response of a cylindrical balloon in the circumferential direction.

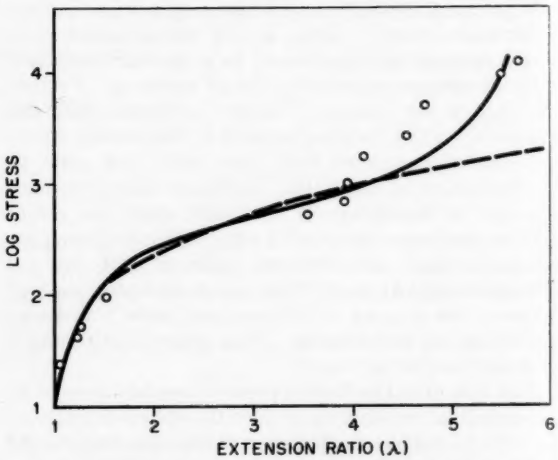

Figure 3. Comparison of the stress-strain behavior of an "ideal" material as given by the dashed curve, a material which obeys the inverse Langevin function as given by the solid curve and experimental points as given by the open circles.

The stress has been plotted on an arbitrary scale, and the two theories have been adjusted to agree with experiment at low values of the strain. As can be seen, the experimental values do show a rise in the force at large strains in semi-agreement with the inverse Langevin approximation. Regardless of the detailed mechanism which permits this rise, its existence does demonstrate that some material limit is operative. This limit is thus manifested as a minimum in the pressure-volume curve which, in turn, indicates a finite "bulge" diameter.

Let us now return to the analogy between the discontinuous inflation of the cylindrical balloon and thermodynamic phase separation. Choosing the boiling of a liquid as the phenomenon with which to make comparisons, we can list the points of similarity as is done in Table 1. Regarding the characteristic quantity, the variation in the quantity of gas required to effect a unit growth of the bulge is a function of construction parameters (i.e., length to diameter ratio and wall thickness in the unstrained balloon) and also of the elastic modulus.

[4] James and Guth, *J. Chem. Phys.*, **11**, 455 (1943).

Table 1. Some Points of Similarity Between a Boiling Liquid and the Discontinuous Inflation of a Cylindrical Balloon

Points of similarity	Boiling liquid	Inflating balloon
Existence of two phases	Liquid and vapor	Non-bulged portion and the bulge
Intensive variable	Temperature	Pressure
Extensive variable	Heat content	Quantity of gas
Characteristic quantity	Heat of vaporization	Amount of gas necessary to effect a unit growth of the bulge

One further point which should be mentioned is the maximum in the pressure-volume curve. This corresponds to super-heating in our analogy, and while it is rarely encountered in practice, it does occur. On the other hand, super-cooling is quite common in crystallization procedures and the pressure-volume maximum corresponds very nicely to this phenomenon.

Acknowledgment

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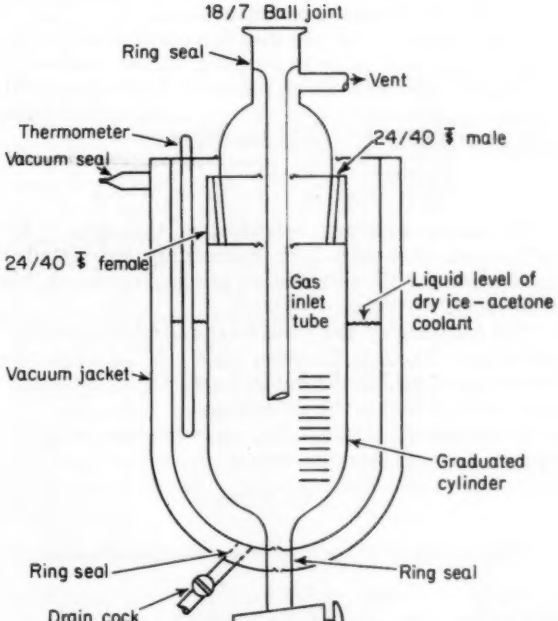
Apparatus for Handling Liquefied Gases

A simple, safe, and useful apparatus was built to facilitate the liquefaction, measurement, and feeding of low-boiling gases in laboratory experiments. The glass apparatus may be economically fabricated by one experienced in glass blowing. It can be used conveniently to condense gases at temperatures −80°–0°C.

In a typical experiment chlorine gas from a pressurized cylinder was fed through the gas inlet tube into the graduated cylinder (see figure). A mixture of dry ice and acetone surrounding the cylinder caused the gas to liquefy. Acetone may be replaced with other low-freezing liquids such as methanol, ethanol, or trichloroethylene. After the desired volume of liquid (in milliliters) was collected at −50°C, the gaseous feed was discontinued. The weight of liquid chlorine in grams was accurately determined by multiplication of the volume by the density of chlorine at −50°C. The frost on the outside of the cold bath sometimes made the volume difficult to read. However, removal of the frost with a cloth dampened in acetone, methanol, or ethanol permitted an accurate reading of the volume. The liquid chlorine at −50°C was then fed dropwise through the stopcock at the desired rate into the reaction flask. Since the solution of the other reactant was at 20–30°C, a cold condenser (filled with dry ice-acetone mixture) was attached to the reaction flask in order to condense any chlorine that might otherwise escape to the atmosphere. The stopcock was lubricated with a silicone stopcock grease.

The use of this new apparatus eliminates the old trial and error method of bubbling the gas through the reaction mixture and weighing periodically until the desired amount has been added. Moreover, gaseous by-products, such as hydrogen chloride, may be liberated during the addition of the chlorine. Since hydrogen chloride is too low-boiling to condense by practical means and is lost to the atmosphere during the reaction, it is impossible to determine the weight of chlorine fed by the old trial and error method. This new procedure also avoids the use of meters which are inaccurate for the measurement of small quantities of gas. Furthermore, certain corrosive gases (such as chlorine and sulfur dioxide) cannot be transferred in the conventional meters because of serious corrosion problems.



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Distribution Coefficients and Ionization Constant of $HAuCl_4$

A radioactive tracer method

Radioactive isotopes of different elements provide rich possibilities for instructive experiments illustrating the laws of physical chemistry and their application.[1] The equilibrium of a substance distributed between two immiscible solvents, a problem of great interest for modern extraction technology, can be easily studied using radioactive tracers.

A good example of an equilibrium of this type is the distribution of chloroauric acid ($HAuCl_4$) between water and an ether. This equilibrium was first studied by Mylius.[2] From one single experimental series, it is possible to estimate not only the distribution coefficient but also the ionization constant of $HAuCl_4$. This can be done if the excess of HCl in the water phase is different in the different experiments.

The mechanism for the distribution of $HAuCl_4$ between water and ether is complex, various molecular species being present in both phases.[3] In this simplified treatment, the following species are assumed to be the only ones present in appreciable amounts:

ether phase: $HAuCl_4$
aqueous phase: H^+, Cl^-, $AuCl_4^-$, $HAuCl_4$

The results obtained indicate that this assumption is correct. Investigations concerning the detailed mechanism for the distribution are in progress at this laboratory.

The following symbols will be used: C'_{Au}, total concentration of gold in the ether phase; C''_{Au}, total concentration of gold in the water phase; C''_{HCl}, total concentration of HCl in the water phase.

Ionization of $HAuCl_4$ in the aqueous phase, in terms of activities, can be represented:

$$K_i = \frac{a_{H^+} \times a_{AuCl_4^-}}{a''_{HAuCl_4}} \tag{1}$$

Distribution of $HAuCl_4$ between the two phases:

$$K = \frac{a''_{HAuCl_4}}{a'_{HAuCl_4}} = \frac{c''_{HAuCl_4}}{c'_{HAuCl_4}} \tag{2}$$

The activity coefficients for $HAuCl_4$ are assumed to be equal to 1, thus $a_{HAuCl_4} = c_{HAuCl_4}$ and

$$C''_{Au} = c_{AuCl_4^-} + c''_{HAuCl_4} \tag{3}$$

If only undissociated molecules are present in the ether phase:

$$C'_{Au} = c'_{HAuCl_4} \tag{4}$$

If both phases have the same volume and if HCl is assumed to remain quantitatively in the water phase, we get:

$$C_{HCl} = c'_{HAuCl_4} + c''_{HAuCl_4} + c_{H^+} \tag{5}$$

If a large excess of HCl is employed, (5) may be approximated by:

$$C_{HCl} = c_{H^+} \tag{6}$$

Combination of equations (2), (3), and (4) gives

$$c''_{HAuCl_4} = K \times C'_{Au} \tag{7}$$

$$c_{AuCl_4^-} = C_{Au''} - K \times C'_{Au} \tag{8}$$

Omitting the activity coefficients for the ions, equation (1) can be written

$$c_{AuCl_4^-} = \frac{K_i \times c''_{HAuCl_4}}{c_{H^+}} \tag{9}$$

Combining (7), (8), and (9) gives

$$C_{Au''} - K \times C'_{Au} = \frac{K_i \times K \times C'_{Au}}{C_{HCl}} \tag{10}$$

which can be written

$$\frac{C''_{Au}}{C'_{Au}} = K + K \times K_i \times \frac{1}{C_{HCl}}$$

In the experiment, C'_{Au} and C''_{Au} are determined at different values of C_{HCl}. If C''_{Au}/C'_{Au} is plotted against $1/C_{HCl}$, a straight line is obtained with the intercept K and the slope $K \times K_i$. Deviations can be expected at high values of C_{HCl} since the ionic strength is not kept constant.

The Radioactive Tracer. About 25 μC Au^{198} was used. This isotope can be produced by irradiation of $AuCl_3$ in an atomic pile. Au^{198} decays, by β- and γ-radiation, with a half life of 2.70 days. The long half life in comparison with the period of measurement has the advantage that, in most cases, no correction for the decay is necessary. On the other hand, the half life is so short that there is no risk for any lingering contamination of the glassware used.

The Experiment

To 80 ml of a $AuCl_3$ solution (4 g $AuCl_3$/l), a small quantity of a solution of radioactive $AuCl_3$ was added. After careful mixing, 5 samples of 5-ml and 5 samples of 10-ml volume were taken out. These were transferred to measuring flasks of 100-ml volume and named sample one–ten according to Table 1. Then, 3 M HCl was added to each and the solutions were diluted to 100 ml with distilled water. The solutions were thereafter transferred to separation funnels together with 100 ml isopropylether. The funnels were shaken for 15 min and the phases allowed to separate for 30 min.

[1] Bleuler, E., and Goldsmith, G. J., "Experimental Nucleonics," Rinehart & Company, Inc., New York, 1952.
[2] Mylius, F., *Z. anorg. Chem.*, **70**, 203–31 (1911).
[3] Saldick, J., *J. Phys. Chem.*, **60**, 500–1 (1956).

The most convenient way of performing the measurements was to use a Geiger-Müller jacketed tube of about 10-ml volume connected to a scaler.[4] The background was determined with the tube filled with both water and ether for 15 min at the operating voltage. The activity of each sample was measured over about 5 min. After each measurement, it was checked that the background had not increased. If this should happen, due to the sorption of gold on the glass walls of the tube, it is necessary to wash the tube with aqua regia.

When calculating the results, it must be kept in mind that the absorption of β-radiation is greater in water than in ether. A correction for this must therefore be applied by multiplying the activity values for the water phase with a factor that is determined in separate experiments with the same amount of gold in water and ether respectively. We obtained the value 1.25 ± 0.02 for this factor which is in very good agreement with the value calculated from what is generally known concerning the absorption of β-radiation in different media. A correction for the background and dead time of the counting system was always made.

Typical Results

In two typical series, the following values were obtained after correction for background and dead time.

Table 1

Sample	HCl, ml, 3 M	$AuCl_3$, ml, 4 g/l	Activity in Water phase, cpm	Activity in Ether phase, cpm
1	5	5	5,401 ± 52	873 ± 10
2	10	5	5,043 ± 50	1,391 ± 15
3	20	5	4,654 ± 48	2,180 ± 21
4	40	5	3,770 ± 44	3,520 ± 33
5	80	5	2,713 ± 26	4,910 ± 45
6	5	10	10,819 ± 105	1,638 ± 16
7	10	10	10,164 ± 102	2,548 ± 25
8	20	10	9,663 ± 68	4,255 ± 37
9	40	10	7,535 ± 60	6,728 ± 58
10	80	10	5,359 ± 38	10,530 ± 107

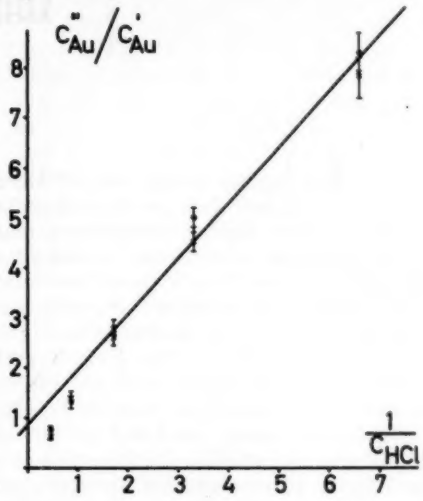
From these results, the following data were calculated:

Table 2

Sample	C_{HCl}	$1/C_{HCl}$	C''_{Au}/C'_{Au}
1	0.15	6.58	7.73 ± 0.40
2	0.30	3.32	4.53 ± 0.20
3	0.60	1.68	2.67 ± 0.13
4	1.20	0.84	1.34 ± 0.09
5	2.40	0.43	0.69 ± 0.05
6	0.15	6.58	8.25 ± 0.40
7	0.30	3.32	4.98 ± 0.20
8	0.60	1.68	2.83 ± 0.13
9	1.20	0.84	1.40 ± 0.10
10	2.40	0.43	0.64 ± 0.05

Figure 1 shows C''_{Au}/C'_{Au} plotted against $(1/C_{HCl})$ (M^{-1}). From this K was found to be 0.85 and K_i 1.35 M. Due to the earlier mentioned deviations expected at high ionic strengths, the values obtained in that region have not been considered.

This experiment has been used for three years in the physical chemistry laboratory course employed at this Institute. The mean values thus obtained from 30 determinations are: $K = 0.6 \pm 0.3$, $K_i = 4 \pm 3$ M. Each determination was, however, based on only three measurements and hence these values were obtained



Distribution of $HAuCl_4$ between water and isopropyl ether plotted against reciprocal of concentration of HCl in water phase.

from correspondingly less accurate values of intercept and slope.

Certain interesting experimental observations have been made. It was found that there is always a certain sorption of gold on all glass walls. If the gold concentration is too small, the values obtained are affected by this sorption. However, when the concentration is kept higher than 0.05 g Au/l, the sorption is not serious. The concentration of HCl should neither be too small nor too high since, otherwise, one phase would be impoverished with respect to gold and this would result in a considerable degree of uncertainty in the activity determination. Each experimental series can be readily performed within 4–5 hrs.

As far as can be seen, no values for the ionization constant of $HAuCl_4$ have been published earlier. The attempts to obtain a more accurate value will be published later.

Acknowledgment

The authors are indebted to Professor Ole Lamm, head of the Division, for his help and never-failing interest in this work.

Valuable discussions with Drs. G. Lundgren and M. Mårtensson are also gratefully acknowledged.

[4] Whitehouse, W. J., and Putman, J. L., "Radioactive Isotopes," Oxford University Press, Inc., London, 1953, or Friedlander, G., and Kennedy, J. W., "Nuclear and Radiochemistry," John Wiley & Sons, Inc., New York, 1955.

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Undergraduate Chemistry Laboratory Fee and Breakage Practices

The rapidly rising cost of laboratory equipment and chemicals has greatly intensified the need for conservative buying, efficient use, and judicious accounting of all materials used in undergraduate chemistry instruction. Even a casual acquaintanceship with current practices will reveal a wide diversity of philosophy, extent, and method of collecting supplementary fees and breakage. The lack of authentic information along these lines prompted the current national study. Nicholson[1] has recently reported the results of a limited survey involving 24 state universities, 43 privately operated institutions, 54 denominational schools, 6 schools operated by municipalities, 2 institutions under federal control, and 3 junior colleges. In the summary of this survey he draws 9 general conclusions, but perhaps his greatest finding and contribution is the discovery of a great diversity of practices, or even a lack of justifiable and consistent policy.

In the present study, a brief questionnaire was prepared and mailed to the chairman of the chemistry department of each of the 250 colleges and universities on the "List of ACS Approved Schools."[2] The prompt and enthusiastic response received indicated a profound interest in this mutual problem. In most instances the details requested were supplied by the chairman of the department or someone closely associated who was equally qualified to provide accurate and complete information. A total of 215 responses was received. This represented 86% of the original mailing. A further tabulation indicated that 98 state tax supported institutions, 74 privately and municipally operated schools, and 43 others, under denominational control, responded to the questionnaire. The great interest in this situation was attested to by the fact that over 25% of the individuals responding requested a tabulation of the findings. Supplementary remarks also indicated that many institutions were still following questionable practices that were inherited from previous administrations, and were now seeking a more logical and justifiable solution.

The original questionnaire included 10 broad categories with subtitles thereto; the results were thus tabulated. It was discovered that 73 schools or 34.0% of the departments collected supplementary laboratory fees for this instruction from undergraduate students enrolled in chemistry. It was also evident that this practice was less common in tax supported institutions. The amount of this collection varied greatly. Of the 73 schools making such a charge, 34 reported a uniform charge for each chemistry course throughout the period of undergraduate instruction. This amount varied from \$2.00 to \$45.00 per course, with an average of \$12.33 and a median of \$10.00. The remaining 39 departments charged a variable amount for different courses with a minimum ranging from \$0.60 to \$30.00 per course, and a maximum ranging from \$2.00 to \$40.00. The minimum average was \$9.12 and the median \$7.50. The maximum average was \$14.21 and the median \$12.00. Of the 73 schools making a fixed or variable laboratory charge, 26 indicated that in general this charge also provided for an average amount of breakage. The remaining 47 institutions had other methods of collecting or ignoring average or excessive breakage. Here the practices were almost as varied as the number of schools responding. Many suggested that the usual laboratory charge, and frequently breakage, if not excessive, was covered in a general university fee, collected from all students. Some collected only for what appeared to be excessive breakage or damage to expensive equipment; or they prorate all breakage among all members of the class. Others frankly admitted that unlimited breakage was common and accepted. Some of the reports indicated supplementary charges for loss of keys or failure to check out. Some schools reported loss of all breakage collections which reverted to other university uses, such as support of athletics. One university made such a charge only during the summer session.

The results indicate that it is a much more common practice to collect chemistry breakage than supplementary laboratory fees. While only 73 schools collected supplementary laboratory fees, there were 109 schools or 50.5% that used some system of collecting laboratory breakage. There were 106 institutions that included such charges in the general laboratory fee or in the university fee.

This supplementary deposit varied from \$1.00 to \$50.00 with an average of \$11.98 and a median of \$5.00. Of this group, 70 made a uniform charge for all chemistry courses varying from \$1.00 to \$30.00, with an average of \$8.40 and a median of \$5.00. The remaining schools varied the required deposit, usually with increased amounts at the more advanced levels of instruction. The method of collecting and administering these breakage collections and deposits followed a rather common pattern, with few deviations. A total of 83 departments employed a system of breakage cards which are usually purchased at the business office at the beginning of each term. In 40 instances the stockroom attendant retained possession of these

[1] NICHOLSON, D. G., J. CHEM. EDUC., 31, 192 (1954).
[2] "Progress Report Number 31 of the Committee on Professional Training," *Chem. Eng. News*, 36, 99–105 (1958).

cards; in 38 cases they remained with the student; and in only 5 schools were they held by the instructor. A system of cash collection for total or excess breakage was followed by 19 institutions. This collection was usually made by the business office at the close of the term. Occasionally the collection was made by the stockroom attendant.

It appears to be the prevailing practice to charge students the actual replacement cost of equipment when the same is lost, damaged, or broken. A total of 127 departments followed this pattern, while 38 others used a "cost plus" system. This "cost plus" varied generally from 5 to 10% and was justified by the usual deterioration, handling, storage loss and breakage, and obsolescence of equipment. Three schools used a fixed breakage charge and 7 others a class average. One unusual situation was encountered wherein students were charged $1/2$ to $1/10$ of the replacement cost, depending upon the course and cost of equipment damaged. It should be noted that the figures quoted regarding the number of schools collecting breakage and charging fixed fees and supplementary breakage do not conflict since so many deviations are employed in assessing and collecting such funds.

The ever present and unsolved mystery of adequate means of collecting excess breakage at the end of the course, regardless of the amount of deposit which is required, seems to persist on most campuses. Various systems have been employed, the most common of which is to withhold grades. This procedure was used by 78 departments, while 38 additional schools refused admission to subsequent chemistry courses. Other plans included exclusion from laboratory, denial of final examination, or refusal to issue college transcripts. Other penalties involve graduation, enrollment in any department of the institution, admission to any subsequent chemistry laboratory, and an additional personal charge to every student as a sort of insurance against such deficiencies.

A number of additional observations and practices were appended to the original questionnaire. One school postponed all billing for supplementary fees and breakage until the end of the year rather than requiring payment or a deposit in advance. Several departments collected only excess breakage beyond a reasonable maximum, whether this amount was covered in a general fee, special fee, or breakage deposit. Some institutions did not collect full value for very expensive equipment, such as Beckmann thermometers, but discounted, or prorated, the cost throughout the entire class. Some instructors believed that the bookkeeping costs did not justify the income received from keeping individual breakage accounts. They usually preferred one general charge including both fee and breakage, or the elimination of all breakage charges. Many institutions increased general tuition charges to all students, whether enrolled in laboratory sciences or not, and simultaneously eliminated most supplementary charges. A few schools assessed a fixed laboratory and breakage fee, based on credit hours or course, and issued no refunds. It appears to be common practice to charge for excessive or careless breakage. Perhaps this tends to discourage extravagance, waste, carelessness, and even mild pilfering. Some colleges included in the survey a comprehensive deposit system, this deposit payable in advance at the business office, which covered laboratory breakage, library fines, athletic equipment, band instruments, and any other property loss or damage to the institution. The department periodically reported student breakage, etc., to the business office. At least three stockrooms sold replacement equipment to the student for cash. Receipts were issued; records were audited periodically; and funds which were collected were credited to the department. One department reported that the abandonment of breakage fees a few years ago, in favor of an all-college comprehensive charge, had greatly encouraged extravagance and carelessness with both chemicals and equipment. A lack of fixed personal responsibility had caused these departments to return again to definite fixed breakage charges. Many schools made supplementary rental charges for the use of balances, weights, platinum-ware, and other expensive items of equipment. Frequently this income was used for repair service or as a reserve for unexpected major breakage.

In addition to the facts and conclusions which are obvious from the tabulations above, the following generalizations seem to emerge as a result of this study:

Tax supported institutions are less inclined to collect supplementary chemistry laboratory and breakage fees than privately supported schools. This is due to factors influencing expected income and support.

The collection of fees for chemistry breakage, and particularly excessive breakage, is a far more prevalent practice than the collection of laboratory fixed fees. The reason is perhaps obvious, for most chemicals used are necessarily expendable, while any loan system of equipment assumes the return of the same in equally usable condition.

Necessary chemicals are usually supplied to students without charge or are included in the laboratory fee.

Many institutions accept a limited or average student breakage without penalty. Careless or excessive breakage is usually charged to the student. A small minority of schools average class breakage, particularly that of expensive items. There is little to recommend this practice for such a procedure hardly encourages care or conservation of chemicals and equipment.

Most breakage charges are computed on a replacement cost or on a "cost plus" basis. The latter is used to cover unavoidable deterioration, depreciation, and loss in storage and handling.

Most schools collecting chemistry laboratory fees or breakage, regardless of the amount or system, reassign all such collections to the department.

An increasing number of institutions are adopting a policy of charging all students an average laboratory or university fee. This obviously does not financially penalize the student enrolled in chemistry or any other laboratory science as contrasted with the non-laboratory student. However, there may be serious complications in such a policy. Several schools reported complete satisfaction with such a system. At least three other departments reported the collection of huge sums under such an arrangement but that they were receiving absolutely nothing in return. While the plan was apparently desirable in theory, the final result was that such collections were diverted to library use, band instruments and uniforms, general college support, and even

athletic activities. While such a plan may have much to recommend it, extreme care should be exercised in its initiation and administration. Funds so collected should be logically allocated and used specifically and only for the purposes collected. Many schools which have tried the system are woefully disappointed and would welcome a return to a departmental plan of responsibility and administration of such funds.

Many departments are adopting newer, simplified, and improved methods of storeroom bookkeeping. This results in tremendous savings, improved operation, and more accurate accounting.

It is observed that careless and inaccurate record keeping, or a complete absence of fixed student responsibility, leads invariably to excessive waste, breakage, and carelessness. Even a class-average breakage system encourages extravagances. Chemistry students, as well as any other responsible citizens, should learn the necessity for caring for and returning or replacing borrowed public property. A fair, reasonable, and equitable system of breakage fees and collections appears to be the best system so far evolved.

* * *

P. R. Story and **C. H. DePuy**
Iowa State College
Ames

A Convenient Atmospheric Pressure Hydrogenation Apparatus

Ordinarily an atmospheric pressure hydrogenation is accomplished by the displacement of hydrogen from a large buret by either mercury or oil. This process requires constant attention and is awkward and expensive except on a small scale. The need to hydrogenate selectively as much as several tenths of a mole of a diene prompted development of a convenient apparatus for quantitative, atmospheric pressure hydrogenations which may be used for large samples.

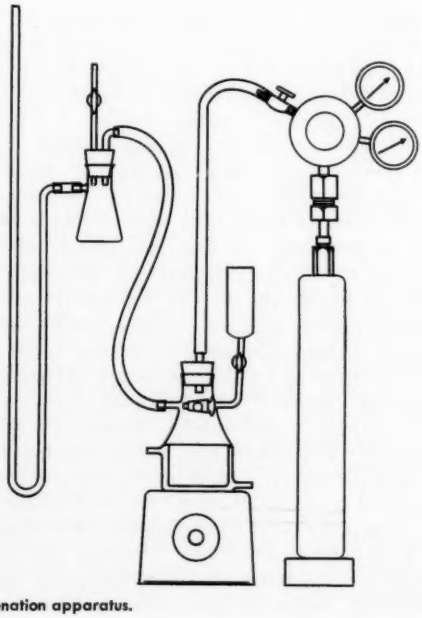
The necessary simple pressure equipment is a lecture bottle which has been equipped with an ordinary pressure regulator. The hydrogenation vessel is a 250-ml Erlenmeyer flask with a water jacket and side arms. A piece of glass tubing serves for a manometer.

To increase the sensitivity of the pressure gauge, the lecture bottle was partially filled with paraffin so that the total volume of the bottle and the bottle pressure gauge was 180 ml. This volume was measured by filling the bottle with acetone and measuring its volume, and also by hydrogenating a known olefin. With a volume of this size, 0.05 mole of an olefin would require 100 psi of hydrogen at 25°C., a quantity that is easily determined on a pressure gauge of 0–400 psi range. The pressure gauge range is, of course, easily changed, depending on the sensitivity and sample size desired. Sensitivity may be increased by reducing the volume of the tank by adding more paraffin, and/or by using a more sensitive pressure gauge.

To calibrate the tank and gauge and to illustrate use of the apparatus, a sample of maleic anhydride was reduced. The catalyst, 200 mg of 5% Pd on charcoal, was prereduced in 25 ml of 95% ethanol. 5 g (0.051 mole) of maleic anhydride, dissolved in 75 ml of 95% ethanol was then drawn into the reaction vessel by application of a slight vacuum from a rubber bulb to the sidearm. The lecture bottle was opened and the needle valve cracked until the manometer showed a slight positive pressure (10–20 mm). The tank pressure (352 psi) was recorded and the magnetic stirrer started. The rate of hydrogenation was followed by periodically closing the lecture bottle and noting the time required for the manometer to fall a given distance. To insure that the fall was due to uptake of hydrogen and not a leak which might have developed in the process, the time required of a change from about +10 mm to −10 mm of Hg was observed. This time was between 3–4 minutes. When hydrogenation was nearly complete, the manometer indicated an increase in pressure in the system. Hydrogenation was complete after six hours with absorption of 102 psi (1250 ml) of hydrogen. Since room temperature was 25°C, the tank and gauge volume is about 180 ml.

The uptake of this quantity of hydrogen in the conventional low pressure hydrogenation apparatus would have required frequent leveling and refilling of a buret.

It is necessary to have an adapter which can be used to fill the lecture bottle from a large tank of hydrogen. This adapter, and the bushing needed to connect the lecture bottle to a pressure regulator, can easily be constructed in a machine shop.



Hydrogenation apparatus.

J. S. Knypl
and R. Antoszewski
University of Łódź
Poland

Method for Determining the Area of Spots in Paper Chromatography

Present methods used to measure the areas of spots in quantitative chromatographic and chemichromatographic analysis are laborious, inaccurate, and dependent on subjective factors. Among these is the planimetric method,[1] the method in which the spots are drawn on coordinate paper,[2] and the method in which the spots, or copies of them, are cut out and weighed.[3] These methods each have their own errors. Some destroy the chromatogram, and none yields permanent records.

The present method uses photography to provide a simple, objective way of measuring the area of a spot in a paper chromatogram.

Between two pieces of glass which have been cleaned with soap and alcohol, there is formed a multiple "sandwich" consisting, from the top down, of the paper with the spot to be tested, under this a piece of transparent drawing paper with a millimeter grid drawn on it, under this the photosensitive material (paper or film), and then the lower glass plate. The whole sandwich is held tightly compressed by two rubber bands. It is illuminated from the top with light, preferably complementary to the color of the spot to be measured. White light may also be used, and in this case, results are improved if a suitable filter is introduced between the paper bearing the spot and the paper bearing the millimeter grid. The time of exposure, depending as it does on the intensity of the light, the type of paper or film used, and the transparency of the sandwich, is chosen by trial.

The accompanying photographs were made by the method described. The lamp used was the ultraviolet lamp, "Minerallight" with filter SL 2537, and a type of photographic paper "Fotopan" C 26° 111 C, made in Poland was employed.

It must be stressed that the conditions of copying must be kept uniform through a series of copies. The length of exposure, as well as the conditions of development of the paper or film, influence the magnitude of the systematic error.

EDITOR'S NOTE: The assistance of Professor Harold G. Cassidy, Yale University, in the preparation of this manuscript is gratefully acknowledged.

[1] SEILER, H., SORKIN, E., AND ERLENMEYER, H., *Helv. Chim. Acta*, **35**, 120 (1952).

[2] LEWANDOWSKI, A., "Chromatografia," red. J. Opieńska-Blauth, Warszawa, P. W. N., **1957**, p. 723.

[3] BEERSTEHER, E., *Anal. Chem.*, **22**, 1200 (1950).

In working with the semicircular spots (Fig. 1) it is suggested that the paper be lengthened at the bottom, using a clean piece of impregnated paper so as to make the millimeter grid more visible. Then the lower edge of the paper should be aligned exactly with one of the heavier lines of the millimeter grid, as shown.

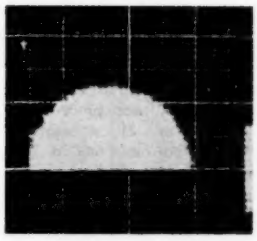


Figure 1. (left) Chemichromatographic spot from a series made in the impregnating technique for determining phosphorus.

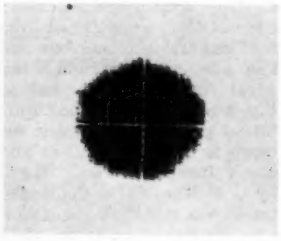


Figure 2. (right) Chemichromatographic spot from the analysis of a protein hydrolysate on paper impregnated with copper orthophosphate.

Good results with fluorescent spots are obtained by using a filter impervious to ultraviolet between the chromatographic paper and the grid. Thus, an inverse image is obtained with the millimeter grid plainly visible on the spot and the rest of the paper remaining white. The photographic paper or film is then preferably chosen to have reduced sensitivity for ultraviolet light. The same results are obtained in recording transparent spots. Of course, in the case of spots which absorb in the ultraviolet or which fluoresce under ultraviolet, the upper plate must pass ultraviolet light. (Fig. 2)

This method gives a permanent record for measurement and calculation of surface area. The subjective element in measuring the spot is reduced to a minimum. The method may be used also to gauge retentiograms. The method has the added advantage that it is independent of any changes in size that the paper or film may undergo during chemical processing, since the scale is subject to the same changes.

The method may be used to measure the areas of other irregular surfaces, such as the surfaces of leaves or of microscopic preparations photographed by the lanametric method, etc.

* * *

Proceedings of the

Pacific Southwest Association of Chemistry Teachers

Summer Conference on the Teaching of Chemistry

The PSACT held its first summer conference on the teaching of chemistry August 16–21, 1959, bringing to fruition the vision of Norris Rakestraw, Norman Kharash, and Dorothy Craig. With Sister Agnes Ann Green at the helm, assisted by Dorothy Craig, plans were completed and funds were secured from the National Science Foundation for partial sponsorship. Asilomar, a beautiful state park on the ocean front of the cool Monterey Peninsula, was chosen as the location.

Hosmer Stone planned the main lecture series, which took place each morning at 9:00 and provided the principal structure about which the conference was arranged. On Monday, George Pimentel of UC spoke on "Infra-red Analysis," and placed it in proper perspective to other spectral methods. He stressed its usage as a modern tool in undergraduate course work at UC. The lecture on Tuesday, "The Chemistry of Bacteria," was given by C. B. Van Niel of the Hopkins Marine Station. The presentation was stimulating, amusing, and very colorful, pointing out how curiosity leads to highly significant information. He illustrated the ability of a few useful principles in correlating a vast array of information in biochemistry. The importance of intuitive reasoning in solving problems was stressed, and the necessity of looking for the unusual was explained in situations such as that in which certain organisms employ protoporphyrin as their nitrogen source. The Wednesday lecture was given by Donald Cram of UCLA on "Recent Advances in Stereochemistry." After an exceptionally clear discussion of the hybridization of atomic orbitals in forming carbon compounds, he illustrated the interpretation of experiments in the field of stereochemistry.

Anton Burg of USC gave the lecture on Thursday. His topic was "Bonding in Boron Compounds and in Inorganic Polymers," and he drew heavily from his own contributions to this field. The constantly unanticipated experimental results yielded information that shed light on various facets of hybridization of orbitals in bonding, particularly in strange situations like pentaborane. The lecture series closed on Friday with Willard Libby of UCLA, who expanded on "Development of Peacetime Uses of Atomic Energy." (See THIS JOURNAL **36**, 627 (1959).)[1]

At 11:15 each morning, discussions dealt with instructional aids in chemical education. Those presenting various aspects were: Elbert C. Weaver of Phillips Academy, Andover, Massachusetts, on "The Film and Film Strip, Uses and Limitations," with the showing of new films for high school and college chemistry courses; Frank Lambert of Occidental College, who presented "New Films on Advanced and Special Topics," such as the Baxter Films, the Pauling Films, and some homemade films on the S_N1 and S_N2 reactions; J. Arthur Campbell, Harvey Mudd College, examined "Lecture Demonstrations and Their Proper Utilization," with huge models of crystalline materials and individual molecules, made from plastic foam materials. Frank Lambert brought along his superb atomic and molecular orbital models, which entranced everyone with their meaningful content when properly used by an experienced manipulator.

Each day at 1:30 P.M., discussion groups were arranged, sometimes separating high school teachers from college and university instructors. One of the highlights was a discussion of the problem of encouraging and identifying latent talent. Due to the inability of Watson Davis, Director of Science Service to attend, Dorothy Schriver presented his speech. "The Science Fair and Similar Programs" was developed by Gretchen Sibley, of the educational division of the Los Angeles County Museum. The problem of gifted students and accelerated class work in general chemistry came under consideration. The pros and cons of the UCLA system, in which two school semesters are utilized in covering three normal semesters of class work, were discussed. Problems of class size in teaching general chemistry received considerable attention. Content of the college general chemistry course also created interest.

At 3:00 P.M. there was planned recreation, as well as displaying of audio and visual aids, and the showing of many films for those wanting more than could be given otherwise. For variety at evening meals, there was a planned barbecue one evening and a banquet another evening. At 7:30 in the evening illustrated travelogues provided interest. G. Ross Robertson showed several of his films from his recent world tour of chemistry laboratories. Teakwood laboratory desks used in Indonesia were among the surprises, as well as interesting pictures of laboratories in Australia and Germany. Hosmer Stone took the group to Alaska and Austria, including some of the activities of the Presbyterian Church in Alaskan education.

At the business meeting toward the close of the conference, new officers were installed. It was concluded that the name of the organization should be The California Association of Chemistry Teachers, since the earlier decision to include teachers from southern Oregon, Nevada, and Arizona did not work out in actual practice. By the time Friday noon had come, it was agreed that the first conference was far more than an experiment; it was a successful reality. The responsibility was transferred to James Ice of San Mateo College, the new PSACT State President, to see that this conference becomes a traditional gathering.

JOHN LEO ABERNETHY
PSACT *Proceedings Editor*

UNIVERSITY OF CALIFORNIA
LOS ANGELES

First PSACT Summer Conference

[1] EDITORS NOTE: Plans are underway for the publication in THIS JOURNAL of most of these lectures.

Report of the New England Association of Chemistry Teachers

Laurence S. Foster

Beginning with this issue, Dr. Laurence S. Foster has stepped down from his post as Editor of the "Report" and Associate Editor of the JOURNAL. A New Englander by birth, education, and marriage, Larry has deep roots in New England soil, yet he has used this devotion to a region to extend his mission, not to limit it.

A graduate of Clark University, in Worcester, Massachusetts, he went to Brown University to study for his doctorate. When this was achieved, in 1926, he remained at Brown to teach general and inorganic chemistry there. In 1943 he left the classroom to join the Manhattan Project at the University of Chicago. When the war was over, he joined the staff of the Watertown Arsenal Laboratories, where he is now Chief, Atomic Energy Division, of the Ordnance Materials Research Office.

Larry began his service to NEACT in 1935, as Chairman of the Southern Division. He was elected President for the 1940–1942 term. In October, 1942, when the pages of the "Report" first began to be printed with the JOURNAL, he was chosen the new Editor. Except for a brief interval beginning in 1944, he has held that post ever since. Nearly every successful activity during these years: Syllabus, Summer Conferences, Student Memberships, to name but a few, have found his name linked as committee member or committee chairman. In 1954, NEACT elected him to Honorary Membership. He has thrown the weight of his influence to other groups, too, especially the Division of Chemical Education, the newly-formed Division of Inorganic Chemistry, and the Northeastern Section of the ACS. He is the co-author of "Chemistry for Our Times," a secondary school text about to appear in its third edition.

We can understand Larry's desire to retire from office, but we accept that fact reluctantly. However, we should feel a great deal worse about it than we do, if we visualized this as a permanent loss. We all know Larry too well to expect him to stop being himself at this point. We are counting on and looking forward to seeing his welcome name many times more as a contributor to our future pages.

ROBERT D. EDDY
Editor, NEACT Report

"We need to develop an intellectual atmosphere at the community level that encourages and recognizes scholarship on the part of both teachers and students; an atmosphere that encourages science-teacher participation in the activities of professional educational and scientific organizations; an atmosphere that allows more time for study, laboratory preparation, guidance of science projects, participation in research, course revision, and similar scholarly activities; an atmosphere that returns to the teacher the role of scholar rather than technician."

—From an Editorial in "Science," October 16, 1959 by ROBERT E. HENZE, *Educational Secretary, American Chemical Society*

Chem Ed

LETTERS

To the Editor:

In the July, 1959, "Chem Ed Letters" M. J. Sienko and R. A. Plane complained about a misinterpretation of a sentence taken from their textbook. If they had written: "Hydrogen ions exist in basic solution but not in appreciable concentration," they would not have given cause for confusion and ambiguity.

Here the authors failed to establish clearly two facts by using the negative approach. If they gave more thought to the semantic value of the positive approach, they would have developed a plainer, simpler, and more orderly style, which is lacking so sadly in our present textbooks.

After all, do we say, "I do not have any appreciable amount of apples?" And wouldn't this lead people to think that "I have no apples?"

A. SIMON

SAN FRANCISCO
CALIFORNIA

To the Editor:

In his review of the second edition of our "General Chemistry" (THIS JOURNAL, **36,** 476 (1959)), Jack W. Eichinger, Jr., calls attention to our use of a modified version of the "Atomic Structure Chart of the Elements" from the first edition of our book. That we had no intention of slighting Dr. Eichinger should be evident in our references to his articles (on pages 102, 128, and 153 of the second edition).

However, we should like to state that we did *not* follow Dr. Eichinger's articles of 1957. Instead, as mentioned on page 101 of our second edition, we followed Gardner (England, 1930), Mazzuchelli (Italy, 1930), Zmaczynski (Russia, 1934), and Ebel (U.S., 1938).

We call readers' attention to the references on page 69 of the excellent little book on the Periodic System by Edward G. Mazurs (60 South Madison Avenue, La Grange, Illinois, 1957). In this book, even "the sloping electron shells" are shown on two of the charts (pages 153 and 155).

W. F. LUDER
ARTHUR A. VERNON
SAVERIO ZUFFANTI

DEPARTMENT OF CHEMISTRY
NORTHEASTERN UNIVERSITY
BOSTON 15, MASSACHUSETTS

✦ ✦ ✦

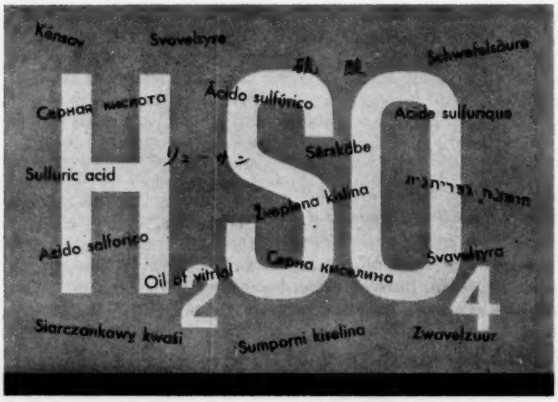
October Cover Re-examined

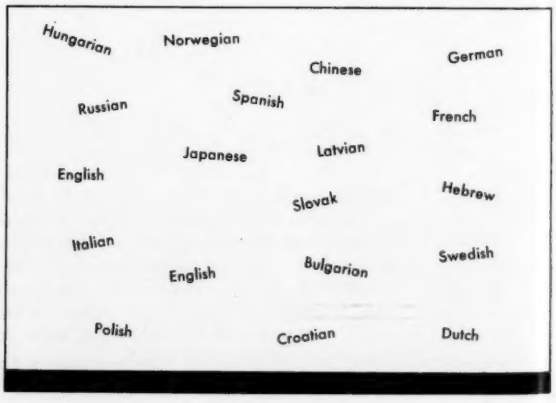
In response to readers' requests, we here publish an identification of the languages illustrated by the October "H_2SO_4" cover. The Editor is grateful for the assistance of Dr. Peter M. Bernays and others of the *Chemical Abstracts* staff.

A letter from Dr. Antoni Z. Zielinski, a visitor at Purdue University from the Technical Institute of Szczecin, Poland, points out that "Siarczankowy Kwasi" is a seriously deformed version of what should be "Kwas siarkowy."

We extend apologies to our Polish friends. The *CA* artist consulted the Polish-English dictionary by Stanistawski published by David McKay, New York, but failed to heed the direction that "czan" should be dropped when "kowy" was added for "sulfuric."

We also apologize to those of our oriental friends who will have to stand on their heads to read the inverted characters in the center.





Chem Ed

BOOK REVIEWS

General Chemistry

P. W. Selwood, Professor of Chemistry, Northwestern University. 3rd ed. Henry Holt & Co., New York, 1959. x + 661 pp. Many figs. 17 × 24 cm. $6.95.

This new edition contains a number of notable changes from previous issues. The first part of the book has been rather extensively recast, giving a smoother introduction. A larger print and more attractive styling is used, with all illustrations redone and enlarged. The basic approach and narrative style characteristic of the second edition is retained, beginning with the concept of atoms, atomic structure and atomic combinations; chemical arithmetic, states of matter, molecules and molecular weights are then discussed, followed by descriptive chemistry of oxygen and hydrogen and a general treatment of the periodic law. Chapters on chemistry and energy, and solutions are then presented, followed by sections on the descriptive chemistry of the non-metals and the metals. The inorganic material is concluded with a chapter on nuclear chemistry. As in the earlier edition the last quarter of the book is devoted to the chemistry of carbon and organic chemistry. This section does not appear to have been changed materially.

The narrative style provides interesting reading although it increases the amount of material to be digested by the student. Many quotes which give a strong historical flavor are included from the works of men eminent in the early development of our science.

To this reviewer, clarity of presentation is one of the strongest points of the book. It is easy to read, the illustrations are excellent, sample problems in the sections involving stoichiometry are well-planned and ample exercises are provided at the end of each chapter.

The chapter on the periodic table and electronic structure has been considerably improved over the second edition. The older use of a ring representation of electronic structure of atoms and molecules has been dropped in favor of modern concepts and the use of dot formulas has been greatly increased.

The author does not use ionic equations as much as seems desirable in discussing reactions which occur in solution. Discussion of the chemistry of the metals is limited largely to metallurgical processes and types of compounds, with very little included concerning solution chemistry of the metals and the problems of complex ion formation. Oxidation-reduction reactions are treated very briefly; half-reaction method of balancing is not discussed.

Users of the Selwood text will find this is not just a token revision but one in which many improvements have been made.

N. W. Gregory
University of Washington
Seattle

Reviewed in this Issue

P. W. Selwood, General Chemistry
H. Flaschka, EDTA Titrations
P. de Mayo, Mono- and Sesquiterpenoids and The Higher Terpenoids
The Science Study Series. Volumes 1–5
Adrien Albert, Heterocyclic Chemistry: An Introduction
D. J. Duffin, Laminated Plastics
Gordon J. Van Wylen, Thermodynamics
Gmelin Institute and *E. H. E. Pietsch*, Editors, Gmelins Handbuch der Anorganischen Chemie. Magnetic Materials: Supplement to System 59, Iron
Herbert W. Cremer and *Trefor Davies*, Editors, Chemical Engineering Practice. Volume 6, Fluid Systems 2
J. F. Danielli, K. G. A. Pankhurst, and *A. C. Riddiford*, Editors, Surface Phenomena in Chemistry and Biology
Arthur R. von Hippel, Molecular Science and Molecular Engineering
Jean Timmermans, The Physico-Chemical Constants of Binary Systems in Concentrated Solutions. Volumes 1 and 2, Two Organic Compounds

EDTA Titrations

H. Flaschka, Georgia Institute of Technology, Atlanta. Pergamon Press, New York, 1959. 138 pp. 10 figs. 14.5 × 22 cm. $6.50

Most textbooks in quantitative analysis devote less than six pages to a discussion of complexometric titrations with (ethylenedinitrilo) tetraacetic acid (EDTA). Yet this single reagent has revolutionized modern inorganic titrimetric analysis. Although several books on analytical applications of amino polycarboxylic acids are available (e.g., "Complexometric Titrations," by G. Schwarzenbach, translation by H. Irving, Interscience, New York, 1957), none of these is particularly suitable for use in an undergraduate chemistry course. The author has written a supplementary textbook based upon extensive research and teaching experience with EDTA titrations which will help fill the growing need for additional reference material on this important subject.

Following a brief historical introduction and qualitative description of chelate formation, the basic theory of complexometric titration curves, metal ion indicators, titration selectivity, and masking is presented. A mathematical derivation of "the apparent stability constant" as a function of *p*H and competing equilibria is discussed in reasonable detail. In a number of cases principles are illustrated by sample calculations and/or simple laboratory experiments. Two chapters describing preparation of reagents and hints for laboratory work will be appreciated by those who wish to avoid the pitfalls that may be encountered in the use of EDTA. In agreement with the author, it has been the experience of the reviewer that improper regard for one or more of the fine points mentioned in this section accounts for most of the difficulties with these titrations. Six chapters are devoted to a survey of the different modes of complexometric titration including detailed procedures for several analyses that may be accomplished by each method. Examples of multicomponent mixtures that may be determined with a standard solution of EDTA are also given. All examples have been chosen from the reactions of about twenty common elements. The final three chapters briefly cover the application of potentiometric and photometric endpoint detection as applied to complexometric titrations. Amperometric, thermometric, and conductometric techniques are mentioned but not discussed. A group of sample questions and problems are included in Appendixes A and B respectively.

For the most part the topics have been wisely selected and carefully developed. References have been inserted at the end of a number of chapters to encourage further study. The discussion of selectivity of complexometric titrations could be improved by introduction of *p*M versus *p*H diagrams. It also appears that the organization of the book might be strengthened if a chapter were written which contained a summary of EDTA chemistry, i.e., kinetic, *p*H, and oxidation state variables found with the common elements. This

information is now scattered throughout the book, frequently appearing in the discussion of laboratory experiments. A start in this direction has been made in Chapter 3, Experiments with EDTA Complexes.

This book will be particularly valuable to teachers of general chemistry or quantitative analysis who wish to extend the presentation of complexometric titrations beyond the usual "water hardness determination" stopping point.

W. H. McCurdy, Jr.
Princeton University
Princeton, New Jersey

Mono- and Sesquiterpenoids

P. de Mayo, Imperial College of Science and Technology, London. (Vol. 2 in the series "The Chemistry of Natural Products," edited by *K. W. Bentley*). Interscience Publishers, Inc., New York, 1959. vii + 320 pp. 16 × 23.5 cm. $7.50.

The Higher Terpenoids

P. de Mayo. (Vol. 3 in the above series). Interscience Publishers, Inc., New York, 1959. vii + 239 pp. 16 × 23.5 cm. $6.

For generations the study of terpenes has engaged the energies and challenged the minds of organic chemists the world over. It is a subject area of wide interest and appeal, filled with an almost staggering variety of intriguing structural problems and often exceedingly complex transformations. The impetus for such investigation has also contributed greatly to the present-day development and application of many important new tools and reactions in organic chemistry.

With the above-titled volumes a newly inaugurated series of intermediate level "texts on the constitution of natural products" makes available at a modest cost a concisely-written but nevertheless well-developed account of the major features of the chemistry of the mono-, sesqui-, di-, and triterpenes (here called "terpenoids").

As in the first monograph of this series, "The Alkaloids," by the Editor, K. W. Bentley [see H. B. Vickery's review, J. Chem. Educ., **35**, 318 (1958)], the typescript text on each left-hand page of the present volumes deals with the Roman-numbered, neatly hand-drawn structural formulas on the right-hand page facing. This arrangement helps to create a pleasing classroom "blackboard atmosphere" while, at the same time, it leaves the text uncluttered by interspersed formulas.

The introductory chapter in the first of these two books offers a brief but extremely useful orientation to the spectral and optical rotational methods that have proved so invaluable in recent years for the determination of structure and configuration in the field of natural products. Acyclic and monocyclic monoterpenoids are then considered in the order of their increasing complexity. In the interests of clarity and pedagogical effectiveness, practically all of the more complicated and many of the simpler reactions are presented and illustrated from the vantage point of modern stereo-electronic theory. Guided in this manner, the uninitiated reader, for whom these texts are primarily intended, is far better equipped to understand and interpret factual aspects of terpenoid chemistry than he would otherwise be.

The discussion of the chemistry of the bicyclic monoterpenoids is especially enhanced by the emphasis placed on the steric requirements of carbonium ion rearrangements in bridged ring systems. Sesquiterpenoids are logically grouped in terms of structural relationships to the cadalene, azulene, or other types of ring skeletons.

The second of these two volumes deals first with the diterpenoids: resin acids and related substances, and a number of more complex representatives, such as marrubiin, cafestol, and columbin. Triterpenoids are then treated: squalene, ambrein, tetracyclic types, α- and β-amyrin-lupeol groups, and miscellaneous classifications. In the final chapter biogenetic relationships, both demonstrated and speculative, are sketched out for all the various classes of terpenoids.

Throughout these two texts the presentation reflects the author's intimate, first-hand knowledge of the subjects covered. Only topics of acknowledged importance are included, but these are well handled. For each structural derivation, all relevant information is carefully marshalled, so that the exposition is made as orderly and logical as possible. Hence, for those who wish to acquire, through a minimum of effort, a reasonably mature grasp of the contemporary view of both classical and modern terpenoid chemistry, these books are warmly recommended.

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The Science Study Series. Volumes 1–5

Doubleday & Company, Inc., Garden City, New York, 1959. Available to secondary school students and teachers through Wesleyan University Press, Inc., Columbus, Ohio. Each volume, 155 pp. 11 × 18 cm. Paperbound. Each, $0.95.

These pocket books bring authoritative treatments of topics in physics to students and the general public. All science teachers will find them valuable and instructive. It is most gratifying to find that eminent physicists whose names are synonymous with their subjects can write so well. The editors and publishers also know their business and have enhanced the offering with simple, clear diagrams and figures and an overall attractive format. The first five titles in the series are: "The Neutron Story" by Donald J. Hughes; "Magnets—the Education of a Physicist" by Francis Bitter; "Soap Bubbles and the Forces Which Mould Them" by C. V. Boys; "Echoes of Bats and Men" by Donald R. Griffin; and "How Old is the Earth" by Patrick M. Hurley.

The books are essays on science subjects written in an almost conversational style, yet by no means superficially. The serious student will wish that references to the original literature had been cited. "Neutrons," "Bats," and "Earth" each include a short list of titles to similar works of a general nature. These three and "Magnets" also have short subject indexes. "Soap Bubbles" is without benefit of either.

W. F. K.

Heterocyclic Chemistry: An Introduction

Adrien Albert, Australian National University, Canberra. Essential Books, Oxford University Press, Inc., New York, 1959. viii + 424 pp. 26 figs. 21 tables. 15 × 22 cm. $9.

Not many short texts covering the heterocyclic field are available, but Albert's presentation differs decidely from any of them. Instead of the conventional arrangement of 3-membered, 4-membered, 5-membered with oxygen, 5-membered with sulfur, 5-membered with nitrogen, preceding the 6-membered heterocycles the present book attempts to correlate heterocyclic chemistry with organic chemistry generally by presenting subject matter in this sequence: heteroparaffinics (as ethylene oxide, tetrahydrofuran, piperidine), π-deficient N-heteroaromatics (as pyridine, quinoline, acridine, pteridine), π-excessive O- and S-heteroaromatics (as furan, thiophene, thiazole, thiadiazole, sydnones), and heteroethylenics (as dihydropyran, pyrroline, pyrazoline, chroman, anthocyanins). The reviewer has long maintained that a graduate course on heterocyclics is important not only for itself but also as a means for reviewing much of aliphatic and aromatic chemistry. Dr. Albert has done an admirable job from this point of view.

An impressive feature of the book is the attention paid to physical properties. Use of infrared and ultraviolet spectra for help in appreciating heterocyclic structures is developed in a special chapter which contains 24 illustrative ultraviolet curves. Another chapter is devoted to ionization constants and the implications of pK_a, while still another chapter deals with oxidation-reduction potentials and dipole moments. Some readers might argue that these matters are outside the scope of a heterocyclic text, but the presentation as given does point concisely and usefully to heterocyclic applications. Also, in this way it becomes certain that the reader is familiar with the inferences intended by the author.

As the author states in the preface "more emphasis is laid on the connection between structure and properties than on methods of synthesis" and "more prominence has been given to parent substances than to their highly substituted derivatives." The book omits consideration of reaction mechanisms.

The reviewer feels that the greatest value of Albert's presentation is to students who are already somewhat familiar with the heterocyclic area. With a good command of syntheses, reactions, and organization of heterocyclic chemistry, a

(Continued on page A38)